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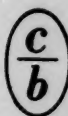
DOKLADY CHEMISTRY

**PROCEEDINGS of the
ACADEMY OF SCIENCES
of the USSR**

Chemistry Section

**ДОКЛАДЫ АКАДЕМИИ НАУК СССР
(DOKLADY AKADEMII NAUK SSSR)**

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АКАДЕМИИ НАУК СССР

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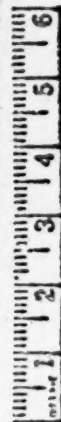
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ABIETIC ACID - A PRIMARY RESIN ACID OF THE OLEORESIN OF THE COMMON PINE (PINUS SILVESTRIS)

I. I. Brady and L. I. Ukhova

(Presented by Academician B. A. Arbuzov, December 8, 1955)

The nature of the major resin acids occurring in the oleo-resin of the common pine, which grows within the boundaries of the USSR, has been established by the investigations of V. V. Shkatelov [1] and V. N.

Krestinsky and co-workers [2]. According to these investigations, dextropimaric (I), levopimaric (II), α -sapinic (III), and β -sapinic acids are the primary resin acids. Actually, there is doubt as to the existence of β -sapinic acid.

The relative content of these acids in the crystalline part of pine oleoresin is, according to N. F. Komshilov [3,4]: I) 18%, II) 36%, and III) 46%.

Abietic acid (IV) has been considered exclusively a secondary acid obtained by isomerization of levopimaric and α -sapinic acids [5]. Actually, abietic acid has been found in the oleoresin of certain American pines [6].

In the present investigation, it was shown that abietic acid is a primary resin acid; it is present in the unchanged oleoresin of the common pine.

The abietic acid was isolated from the oleoresin by means of a method involving crystallization of bornylamine salts of resin acids [7].

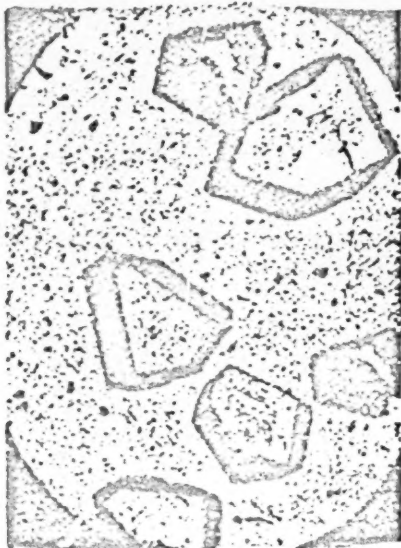
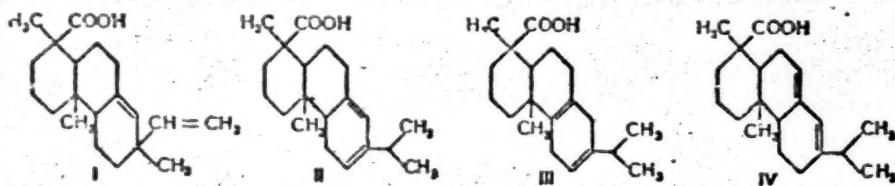


Fig. 1. Photograph of abietic acid crystals.



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EXPERIMENTAL

1100 g of resin acids, separated from fresh oleoresin, was recrystallized from alcohol. After separation of the first fraction of crystals (50%), a second fraction (10%) separated out, from which abietic acid was obtained.

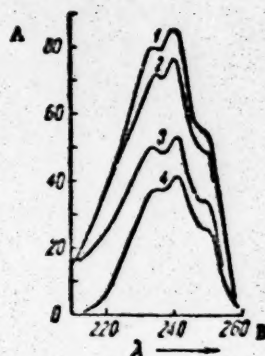


Fig. 2. Ultraviolet absorption spectra. Abietic acid samples: 1) ours, 2) Harris [6]. Bornyl abietate samples: 3) pure, 4) fraction a.

Upon neutralization of the acids of the second of the fraction with bornylamine in ether solution, the salt of levopimaric acid precipitated. After separating this precipitate from the mother liquor, a second fraction of crystals (a) precipitated (10 g), which comprised chiefly bornyl abietate (m.p. 140-145° and $[\alpha]_D = -41.0^\circ$ in alcohol solution). Five crystallizations of this salt fraction from alcohol increased the melting point as follows: 158-159°; 160-160.6°; 160-161.5°; 161.5-162°; 161.5-162°. A total of 2.2 g of salt was obtained.

Decomposition of the salt with boric acid and recrystallization from warm alcohol yielded very well formed crystals of low melting abietic acid (see Figure 1) with a m.p. of 173-174.5° and $[\alpha]_D = -166.7^\circ$ (in absolute alcohol).

Found %: C 79.13, 79.28; H 10.10, 10.00
 $C_{20}H_{30}O_2$. Calculated %: C 79.47; H 9.90

Absorption spectra, in the ultraviolet region of spectrum, of abietic acid are presented in Figure 2.

As seen from the figure, our sample was purer than that described in the literature[6].

Institute of Chemistry Academy of
 Sciences BSSR

Received December 3, 1955

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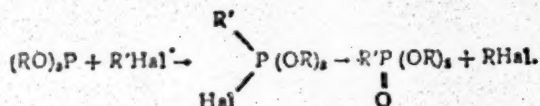
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ON THE ADDITION OF TRIALKYL PHOSPHITES TO CERTAIN UNSATURATED ACIDS

Gilm Kamai and V. A. Kukhtin

(Presented by Academician A. E. Arbuzov, December 12, 1955)

The reaction, discovered fifty years ago by A. E. Arbuzov [1], by which completely esterified phosphorous acids are transformed into esters of phosphinic acids by the action of alkyl halides has been, up to the present time, one of the most important methods of synthesis of various phosphinic esters. This reaction, which is well known under the name of the "Arbuzov rearrangement", proceeds according to the following scheme:



For some time past, considerable importance has also been attached to a new method for synthesizing esters of phosphinic acids, this method being one developed by A. M. Pudovik [2]. This method consists of the addition of acid esters of phosphorus, phosphinic, and thiophosphorous acids to various unsaturated compounds in the presence of sodium alcoholates. As shown by V. S. Abramov [3], the addition of dialkylphosphorous acids to the carbonyl group of aldehydes and ketones proceeds in similar manner. Continuing his investigations in this field, V. S. Abramov established that not only the acid esters of phosphorous acids, but also their total esters, can add to aldehydes; whence, this reaction is related to the rearrangement of pentavalent phosphorus compounds, and is analogous to the Arbuzov rearrangement [4].

In earlier published work [5], we showed that trialkyl phosphites enter into reaction with acid anhydrides, and this reaction also proceeds analogously to the Arbuzov rearrangement. Continuing our investigations in this field, we observed that maleic anhydride, in contrast to the other anhydrides studied by us, reacts with trialkyl phosphites far more actively. The reaction begins at room temperature and proceeds with great evolution of heat, while the anhydrides of saturated acids react at temperatures above 100°. Such an abnormal course of reaction gives rise to the assumption that, in the case of maleic anhydride, first of all the double bond enters into reaction with the trialkyl phosphite. Unfortunately, the products of this interaction resinify during the reaction and distillation, and we were unsuccessful in isolating them in the pure form.

The study of the reaction of trialkyl phosphites with unsaturated acids showed that total esters of phosphorous acid add rather easily to these acids. The addition of trialkyl phosphites to acrylic acid proceeds at room temperature with considerable evolution of heat (up to 100° and higher) by the reaction mixture. Methacrylic acid begins to react with trialkyl phosphites at 60-70°, and the temperature rapidly rises to 100-150°. The addition also proceeds without heating at room temperature when the mixture of reagents stands for a period of several days.

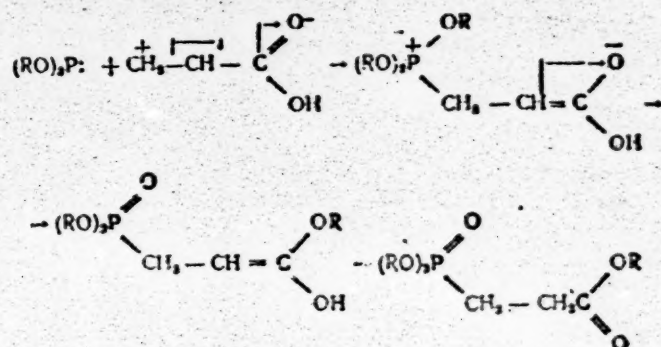
Investigation of the addition products obtained showed that they did not contain a double bond or an acid group, and did not give a reaction for trivalent phosphorus.

Upon saponification of the products of the addition of trialkyl phosphites to acrylic acid, β -phosphonopropionic acid, described earlier by A. E. Arbuzov [6] and A. N. Pudovik [7], was obtained. The melting point of

the acid obtained was 168°, which is identical with the earlier value. Saponification of the products of the addition of trialkyl phosphites to methacrylic acid gave a syrup which did not crystallize for a long time. The material obtained from the reaction of triethyl phosphite with methacrylic acid had physical constants and a boiling point similar to those previously given by A. M. Pudovik [2] for the ethyl ester of β -phosphonoisobutyric acid.

The ethyl ester of β -phosphonopropionic acid obtained by us was described earlier by A. E. Arbuzov and A. A. Daulin [8]. The constants of this ester were identical with those given earlier.

All these data, and also the analytical results, indicate that the addition of trialkyl phosphites to unsaturated acids yields the total esters of the corresponding β -phosphonocarboxylic acids. The mechanism of the addition reaction can be expressed as follows:



The possibility of another reaction mechanism proceeding through a preliminary transesterification of the components with the formation of the dialkylphosphorous acid and the ester of the unsaturated acid seems less probable to us, since dialkylphosphorous acid does not add to acrylates under these conditions without a catalyst.

TABLE 1

Formula	B.p., °C., and pres- sure in mm Hg	n_D^{20}	d_4^{20}	P, %		MR _D	
				found	calc.	found	calc.
$(\text{C}_2\text{H}_5\text{O})_3\text{P}-\text{CH}_2-\text{CH}_2\text{COOC}_2\text{H}_5$	123-124/3	1.4310	1.0941	13.17	13.02	56.31	56.26
$\beta-(\text{C}_2\text{H}_5\text{O})_3\text{P}-\text{CH}_2-\text{CH}_2\text{COOC}_2\text{H}_5 \cdot n$	147-149/4	1.4382	1.0024	9.73	9.62	84.33	84.00
$(\text{C}_2\text{H}_5\text{O})_3\text{P}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{COOC}_2\text{H}_5$	123-125/5	1.4335	1.0761	12.32	12.28	61.09	60.90
$n-(\text{C}_2\text{H}_5\text{O})_3\text{P}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{COOC}_2\text{H}_5 \cdot n$	153-155/3	1.4390	1.0019	9.51	9.23	88.41	88.62
$i-(\text{C}_2\text{H}_5\text{O})_3\text{P}-\text{CH}_2-\text{CH}(\text{CH}_3)-\text{COOC}_2\text{H}_5 \cdot i$	155-157/5	1.4375	0.9911	9.33	9.23	88.82	88.62

Using the above-described reaction, we synthesized the ethyl and butyl esters of β -phosphonopropionic acid and the ethyl, butyl, and isobutyl esters of β -phosphonoisobutyric acid, the butyl esters being synthesized first. The constants of these compounds are given in Table 1.

The reaction, discovered by us, of the addition of trialkylphosphites to unsaturated compounds extends the existing methods for the preparation of esters of phosphinic acids. Mariya Vlad took part in the execution of the experimental part of this work, for which the authors express their appreciation.

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S. M. Kirov Chemical-
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* T.p. = C. B. Translation pagination.

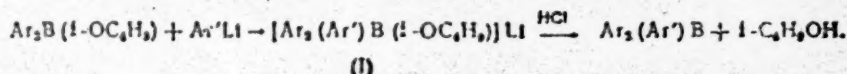
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ORGANOBORON COMPOUNDS. SYNTHESIS OF COMPLEX COMPOUNDS OF UNSYMMETRICAL TRIARYLBORONS

B. M. Mikhailov and V. A. Vaver

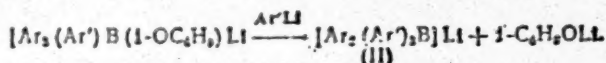
(Presented by Academician B. A. Kazansky, December 21, 1955)

Having set for ourselves the problem of preparing triarylboron compounds, we undertook a study of the reaction between aryllithium compounds and esters of diarylboric acids, which are prepared by a Grignard reaction with trialkylborates [1,2]. It was hypothesized that the lithium salts of triaryloxyborinic acids (I) formed by this reaction would be decomposed by hydrogen chloride into unsymmetrical triarylboron compounds according to:



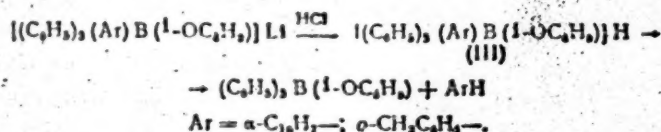
Experiments showed that formation of the borinic acid salts (I) proceeds comparatively smoothly, although accompanied by side reactions. Two salts - lithium diphenyl- α -naphthylisobutoxyborinate (I, $\text{Ar} = \text{C}_6\text{H}_5-$, $\text{Ar}' = \alpha\text{-C}_{10}\text{H}_7-$), which was formed by the action of α -naphthyllithium on the isobutyl ester of diphenylboric acid, and lithium di- α -naphthylphenylisobutoxyborinate (I, $\text{Ar} = \alpha\text{-C}_{10}\text{H}_7-$, $\text{Ar}' = \text{C}_6\text{H}_5-$), which was formed by the action of phenyllithium on the isobutyl ester of di- α -naphthylboric acid - were individually isolated. In three other cases (the lithium salts of diphenyl-*o*-tolylisobutoxy-, triphenylisobutoxy-, and di- α -naphthyl-*o*-tolylisobutoxyborinic acids) the complexes were not isolated, and further operations were carried out with the ethereal solutions obtained directly in the reaction.

The borinate salts (I) can enter into a reaction with aryllithium compounds, exchanging the alkoxy group in the complex anion for an aryl radical and thereby being converted into tetraaryl derivatives of borinic acid.



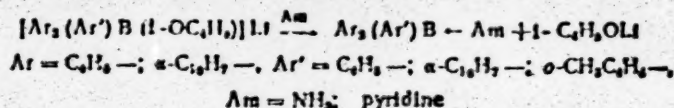
Thus, in experiments on the action of phenyllithium or *o*-tolyllithium on esters of diphenylboric acid, the corresponding lithium salts of tetraphenyl- and diphenyl-di-*o*-tolylborinic acid (II, $\text{Ar} = \text{C}_6\text{H}_5-$, $\text{Ar}' = \text{C}_6\text{H}_5-$, $\text{Ar}'' = \text{C}_6\text{H}_5-$ or $\text{CH}_3\text{C}_6\text{H}_4-$) were also obtained in small amounts in addition to the salts (I).

Since there are indications in the literature that triarylborons (triphenylboron) are hydrolyzed by the action of hydrochloric acid [3], decomposition of the complexes (I) in aqueous solution was unsuitable. Therefore, the salts (I) were converted into triarylborons by decomposition with dry hydrogen chloride according to the method used by one of us and P. M. Aronovich for the preparation of the ester of diphenylboric acid from lithium diphenyl-diisobutoxyborinate [4]. In the remaining experiments on the action of dry hydrogen chloride on the salt (I), an ester of diarylboric acid was obtained instead of a triarylboron. Thus, for example, the isobutyl ester of diphenylboric acid, and not the expected diphenyl- α -naphthylboron and diphenyl-*o*-tolylboron, were obtained from the lithium salts of diphenyl- α -naphthylisobutoxy- and diphenyl-*o*-tolylisobutoxyborinic acids.



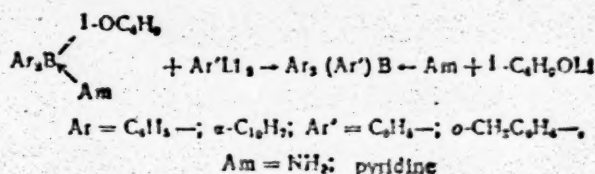
Thus, in the cases cited, anions of the α -naphthyl and α -tolyl radicals, which occupy an average position between phenyl and alkoxy groups with respect to electronegativity, and not the more electronegative alkoxy group, were separated from the complex anion of the acid (II) and joined to a proton.

Cleavage of the lithium salts of the triarylisobutoxyborinic acids (I) with maintenance of the triarylboron grouping was successfully carried out by the action of ammonia or pyridine on the salt (I). In all cases, a molecule of amine displaced an alkoxyl ion from the complex anions resulting in the formation of neutral ammine complexes of mixed triaryl compounds of boron and a lithium alcoholate.



Both the ammoniates and pyridinates of the triarylborons were insoluble in water and, therefore, were easily separated from the alcoholate.

Ammine complexes of triarylboron compounds were obtained by the action of aryllithiums on ammine complexes of esters of diarylboric acids according to the equation:



EXPERIMENTAL

Lithium diphenyl- α -naphthylisobutoxyborinate. Diphenyl- α -naphthylboron ammine. A solution of 16.6 g (0.07 mole) of the isobutyl ester of diphenylboric acid [1] (b.p. 122-122.5°, 2mm, density 0.9760) in 30 ml of absolute ether was added, over a period of 1 hour and with vigorous stirring, to an ethereal solution of α -naphthyllithium (0.07 mole) at -10°. The reaction mixture was stirred for 2 hours at room temperature, after which the resulting crystalline precipitate was filtered, washed several times with small portions of absolute ether, and dried under vacuum. 9.65 g (30% of theoretical) of the dietherate of lithium diphenyl- α -naphthylisobutoxyborinate was obtained.

Found %: C 78.12; H 8.25; B 2.24; Li 1.47
C₂₀H₂₀BOLi. Calculated %: C 77.92; H 7.85; B 2.24; Li 1.50

A stream of dry ammonia was passed through the filtrate obtained after separation of the dietherate of the lithium salt. The ammoniate obtained was recrystallized from a mixture of benzene and pentane (1:1). The yield of the ammoniate of diphenyl- α -naphthylboron (m. p. 185-187°) was 6.20 g (30% of theoretical, calculated on the basis of the diphenylboric acid ester).

Found %: C 84.24; H 6.40; B 3.55; N 4.59
C₂₂H₂₂BN. Calculated %: C 85.45; H 6.52; B 3.50; N 4.53

Lithium di- α -naphthylphenylisobutoxyborinate. The experiments were carried out in a manner analogous to the preceding. 0.28 mole of phenyllithium, free from lithium bromide [5], and 9.40 g (0.028 mole) of the isobutyl ester of di- α -naphthylboric acid [2] were used. The complex was precipitated by n-hexane from a concentrated ethereal solution. 9.50 g (80%) of crystalline lithium borinate was obtained.

Found %: B 2.44; Li 1.64
C₂₀H₂₀BOLi. Calculated %: B 2.52; Li 1.65

Diphenyl- α -naphthylboron pyridinate. To a solution of 0.9 g of the dietherate of lithium diphenyl- α -naphthylisobutoxyborinate in a mixture of 30 ml of absolute ether and 10 ml of absolute benzene was added 0.5 ml of pyridine. The solution was evaporated to dryness under vacuum, and 30 ml of water was added to residue. The pyridinate, which was insoluble in water, was filtered, washed with water, and dried at 50° under vacuum. 0.63 g (68% of theoretical) of diphenyl- α -naphthylboron pyridinate, with a m.p. of 170-175°, was obtained.

Found %: B 2.90; N 3.85
 $C_{27}H_{22}BN$. Calculated %: B 2.91; N 3.77

Di- α -naphthylphenylboron pyridinate. Using the preceding method, 1.10 g (80% of theoretical) of di- α -naphthylphenylboron pyridinate, having a m.p. of 213-215°, was obtained from 1.40 g of lithium di- α -naphthylphenylisobutoxyborinate and 0.50 g of pyridine.

Found %: B 2.52; N 3.49
 $C_{22}H_{14}BN$. Calculated %: B 2.57; N 3.32

Di- α -naphthyl-*o*-tolylboron pyridinate. From 0.011 mole of *o*-tolyllithium and 0.011 mole of the isobutyl ester of di- α -naphthylboric acid, by treatment of the resulting lithium salt solution with 1.5 ml of pyridine, was obtained 2.25 g (46% of theoretical) of di- α -naphthyl-*o*-tolylboron pyridinate, m.p. 203-205°.

Found %: B 2.57; N 3.25
 $C_{22}H_{14}BN$. Calculated %: B 2.48; N 3.22

Di- α -naphthylphenylboron ammine. A stream of dry ammonia was passed through 2.15 g of lithium di- α -naphthylphenylisobutoxyborinate in 30 ml of absolute ether. The ether was evaporated under vacuum, and the residue diluted with water. The dinaphthylphenylboron ammine was filtered, washed with water, and dried at 50° under vacuum. The yield of ammine was 1.35 g (75% of theoretical), m.p. 170-173° (sintering at 135-144°).

Found %: C 87.18; H 6.66; B 2.95; N 3.47
 $C_{26}H_{22}BN$. Calculated %: C 86.92; H 6.17; B 3.01; N 3.90

Diphenyl-*o*-tolylboron ammine. Potassium diphenyldi-*o*-tolylborinate. From 0.052 mole of *o*-tolyllithium and an equimolar amount of the isobutyl ester of diphenylboric acid was obtained, by the preceding procedure with subsequent treatment of the ethereal solution of the lithium salt with ammonia, 1.23 g (54.5% of theoretical) of diphenyl-*o*-tolylboron ammine, m.p. 175-178° (sintering at 147-150°).

Found %: C 83.50; H 7.42; B 4.18; N 5.27
 $C_{21}H_{20}BN$. Calculated %: C 83.53; H 7.38; B 3.96; N 5.13

0.11 g of colorless, crystalline potassium diphenyldi-*o*-tolylborinate was obtained from the filtrate by precipitation with potassium bromide.

Found %: B 2.85
 $C_{26}H_{24}BK$. Calculated %: B 2.60

Triphenylboron ammine. Potassium tetraphenylborinate. By the preceding method, 1.20 g (65% of theoretical) of triphenylboron ammine, m.p. 202-204° [6], was obtained from 0.05 mole of phenyllithium and an equimolar amount of the isobutyl ester of diphenylboric acid. 0.1 g of potassium tetraphenylborinate [7] was precipitated from the filtrate with a solution of potassium bromide.

Found %: B 3.04
 $C_{24}H_{20}BK$. Calculated %: B 3.02

The action of hydrogen chloride on lithium diphenyl-*o*-naphthylisobutoxyborinate. 5.82 g of the dietherate of complex was dissolved in 30 ml absolute benzene; a stream of dry HCl was passed through the solution. The solution was filtered, and the benzene was evaporated under vacuum. The residue was dissolved in pentane and treated with dry ammonia. 3.12 g (97% of theoretical) of the ammoniate of the isobutyl ester of diphenylboric acid, m.p. 101-103°, was obtained. After evaporation of the solvent, 1.10 g of naphthalene, m.p. 79-80°, was obtained from the filtrate. The ammoniate of the isobutyl ester of diphenylboric acid was obtained in 88% yield by the action of ammonia on a pentane solution of the diphenylboric acid ester. M.p. 103-105° (m.p. 64-67°, according to the data of Letsinger [8]).

Found %: C 75.25; H 8.74; B 4.19; N 5.32
 $C_{16}H_{22}BON$. Calculated %: C 75.24; H 8.69; B 4.24; N 5.49

The action of hydrogen chloride on lithium diphenyl-*o*-tolylisobutoxyborinate. The ethereal solution of the complex obtained from 0.027 mole of *o*-tolyl lithium and 6.40 g (0.027 mole) of the isobutyl ester of diphenylboric acid was treated with dry hydrogen chloride. 4.80 g (70%) of the ammoniate of the isobutyl ester of diphenylboric acid, m.p. 103-105°, and 1.5 ml of toluene were isolated.

The reaction of the ammoniate of the isobutyl ester of diphenylboric acid with phenyllithium. To an ethereal solution of 0.0074 mole of phenyllithium was added a suspension of 1.88 g (0.0074 mole) of the ammoniate in 25 ml of absolute ether. The ether was evaporated under vacuum, and the residue treated with water. 1.03 g (50%) of triphenylboron ammine, m.p. 203-205 [5], was obtained.

The action of aryllithiums on the isobutyl esters of diarylboric acids in the presence of pyridine. To an ethereal solution of 0.005 mole of phenyllithium was added, without cooling, a solution of 1.01 g (0.0043 mole) of the isobutyl ester of diphenylboric acid and an equimolar amount of pyridine in 5 ml of absolute ether. Precipitation of crystals of triphenylboron pyridinate began after several minutes. The ether was evaporated under vacuum, and the residue treated with water. 1.30 g (96%) of triphenylboron pyridinate [6], decomposing at 215°, was obtained.

Found %: B 3.30
 $C_{12}H_{22}BN$. Calculated %: B 3.36

Diphenyl-*o*-tolylboron pyridinate, m.p. 172-174°, was prepared by this same method in 87% yield.

Found %: B 3.23
 $C_{20}H_{22}B$. Calculated %: B 3.33

Di-*o*-naphthyl-*o*-tolylboronpyridinate (m.p. 203-205°, 85% yield) was also prepared.

All operations connected with the study of the reaction of esters of diarylboric acids with aryllithiums and with the decomposition of the lithium complexes were carried out in an atmosphere of dry nitrogen.

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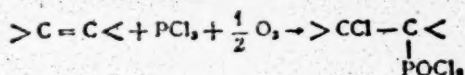
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OXIDATIVE CHLOROPHOSPHINATION OF CHLORO SUBSTITUTED OLEFINS

L. Z. Soborovsky, Ye. M. Zinov'yev and L. I. Muler

(Presented by Academician I. L. Knunyants, December 22, 1955)

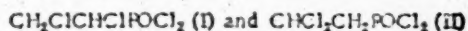
During oxidative chlorophosphination* of olefins with phosphorous trichloride there are formed the corresponding acyl chlorides of chloroalkane phosphinic acids [1].



Certain facts, observed while carrying out reactions of phosphorus trichloride and oxygen with propylene, indicated the formation, along with the compound $CH_3CHClCH_2POCl_2$, of its isomer $CH_3CH(CH_2Cl)POCl_2$. However, conclusive proof of this was not obtained.

It was, therefore, expedient to investigate oxidative chlorophosphination of substituted olefins, which would make it possible to trace more clearly the direction of addition during their reaction with phosphorus trichloride and oxygen. In the present work, the behavior of two chloro derivatives of the ethylene series, vinyl chloride and allyl chloride, under oxidative chlorophosphination conditions was investigated.

We showed that vinyl chloride, during the reaction with phosphorus trichloride and oxygen, forms a mixture of isomeric acyl chlorides of dichloroethane phosphinic acid.



It was not possible to isolate individual compounds from the reaction mixture by ordinary fractionation, since the mixture distilled within a narrow temperature interval (see Table 1).

The presence of isomers was shown by a series of transformations, to which the mixture of acyl dichlorides was subjected. By the action of an excess of butyl alcohol at -5° , the previously prepared acyl chlorides were converted into the corresponding esters



which, just as did the original acyl chlorides, distilled within narrow limits. Upon subsequent treatment of these esters with triethylamine at 20° , one of the isomers in the mixture easily split out hydrogen chloride, forming the butyl ester of 2-chloroethylenephosphinic acid (V), while the other isomer remained unchanged. The marked difference in the boiling points of compounds (III) and (V) permitted separation of the individual substances from the mixture. Only 30-35% of the original mixture of esters of dichloroethane phosphinic acid (VD) reacted with the triethylamine, 65-70% remaining unchanged in spite of the use of an excess of amine and an increase in the dehydrochlorination temperature to $60-70^\circ$.

That the unchanged compound was the dibutyl ester of 1,2-dichloroethane phosphinic acid (V) was established by dehalogenation with zinc dust to the dibutyl ester of ethylenephosphinic acid (VII).

The results obtained show that the other isomer contained in the mixture (treated with triethylamine) was the ester of 2,2-dichloroethane phosphinic acid (IV).

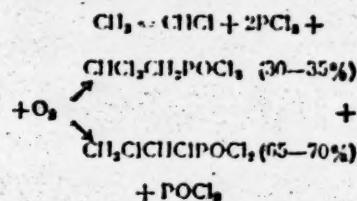
* By "oxidative chlorophosphination reaction" we designate the interaction, reported by us, of hydrocarbons (or their derivatives), oxygen, and PCl_3 (or products of partial substitution of Cl by organic residues), which results in formation of a phosphorus-carbon bond, formation of acyl chlorides of corresponding alkane phosphinic acids, and conversion of trivalent phosphorus compounds into pentavalent compounds [1-4].

TABLE
Properties of Synthesized Compounds

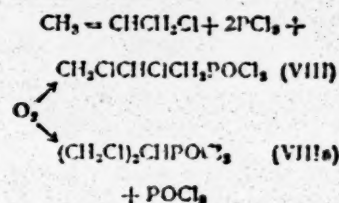
Compound	Formula	B.p., °C	Pressure, mm Hg	d ₄ ²⁰	n _D ²⁰	M _D ²⁰		Yield, %	Notes
						found	calc.		
(I)	CH ₂ ClCHClPOCl ₂	208-210	750	1.5376	1.4998	38.79	39.22	68*	Mixture of isomers
(II)	CHCl ₂ CH ₂ POCl ₂	74-75	2.5	—	—	—	—	—	—
(III)	CH ₂ ClCHClPO(OC ₂ H ₅) ₂	143-145	3	1.1548	1.4402	67.62	68.08	—	—
(IV)	CHCl=CHPO(OC ₂ H ₅) ₂	119-120	4	1.0712	1.4502	63.89	63.65	74*	Mixture of isomers (III) and (IV)
(V)	CH ₂ Cl ₂ PO(OC ₂ H ₅) ₂	134-136	3	1.1583	1.4510	67.34	68.98	—	—
(VIII)	CH ₂ =CHPO(OC ₂ H ₅) ₂	101-102	1.5	0.9737	1.4300	58.23	58.78	—	Possible presence of (CH ₂ Cl) ₂ CHPOCl ₂ (VIIIa)
(VIII)	CH ₂ ClCHClCH ₂ POCl ₂	104-107	3	1.5801	1.5073	43.40	43.80	79	—
(IX)	CH ₂ ClCHClCH ₂ PO(OC ₂ H ₅) ₂	110-118	3	1.2457	1.4570	51.45	53.18	80	—
(X)	CH ₂ =CHCH ₂ PO(OC ₂ H ₅) ₂	90-91	12	1.0390	1.4312	41.41	44.40	17	—
(XII)	CH ₂ ClCHClCH ₂ PO(OC ₂ H ₅) ₂	110.5-111.5	3	1.3337	1.4683	45.35	45.85	71	—
(XIII)	CH ₂ ClCHClCH ₂ PO(OC ₂ H ₅) ₂	137-140	2	1.2810	1.4709	62.08	62.01	72	—
(XIV)	CH ₂ ClCHClCH ₂ PO(OH) ₂	mp 67-68*	—	—	—	—	—	—	—

* Total yield of the mixture of isomers.

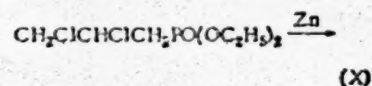
Thus, the oxidative chlorophosphination of vinyl chloride under our conditions proceeds in two directions.



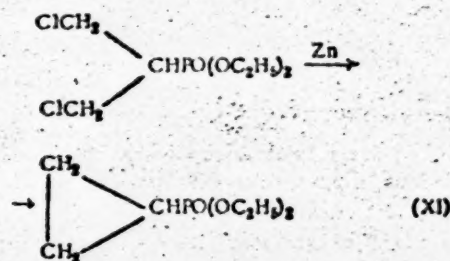
Oxidative chlorophosphination of allyl chloride leads to the formation of the acyl chloride of dichloropropanephosphinic acid. It might be expected that, in this case also, the process proceeds in two directions:



From the reaction mixture was isolated a substance, the structure of which was established by the following transformations. The acyl chloride of dichloropropanephosphinic acid was converted into the diethyl ester of this acid (IX) by the action of an excess of alcohol at 0°. The ester thus obtained was subjected to dehalogenation by zinc dust in ethanol. Depending on the structure of the original acyl chloride, it might be expected that there would be formed the diethyl ester of 1-propene-3-phosphinic acid (X)



or the diethyl ester of cyclopropanephosphinic acid (XI)



or a mixture of the isomeric compounds (X) and (XI)

The isolated ester easily absorbed bromine. Elementary analysis and a comparison of the constants of this diethyl ester with the constants of the diethyl ester of allylphosphinic (1-propene-3-phosphinic) acid, prepared by the method of A. E. Arbuzov from triethyl phosphite and allyl bromide, and also with the literature data [5-7] indicated that the isolated compound was compound (X).

The structure of the compound obtained was also confirmed by its infrared spectrum, in which was observed the characteristic frequency of double bonds $\nu_{C=C}$ (1620 cm^{-1}).*

However, the low yield of compound (X) does not permit the assertion, with complete authenticity, that oxidative chlorophosphination of allyl chloride proceeds only in one direction.

In addition to the ethyl ester of dichloropropanephosphinic acid, the methyl (XII) and allyl (XIII) esters were also synthesized. Moreover, dichloropropanephosphinic acid (XIV) was prepared from the acyl dichloride of dichloropropanephosphinic acid [dichloropropanedichlorophosphine oxide].

The oxidative chlorophosphination of vinyl chloride and allyl chloride was carried out by passing oxygen through a mixture of the respective chloroolefin and phosphorus trichloride at low temperatures, which maintained the halo derivative entering into the reaction in the liquid state (-20° and $+15^\circ$, respectively).

The relatively high yields of oxidative chlorophosphination products in both cases of reaction with halogenated olefins are deserving of mention (especially on comparison of these yields with those obtained from the corresponding hydrocarbons, ethylene and propylene).

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* The infrared spectrum of the material was obtained by S. S. Dubov.

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ETHERATES AND DIOXANATES OF ORGANOLITHIUM COMPOUNDS

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K. A. Kocheshkov

Complex organometallic compounds, as a class, have acquired, at the present time, great theoretical and practical importance. To a considerable degree, this applies also to organometallic compounds of the alkali metals.

We considered it necessary to report, in the present article, on the properties of some etherates and dioxanates* of individual organolithium compounds and on methods for their preparation in a pure form.

This class of complexes of organolithium compounds with ethers was discovered by Grosse (1929), for example, the dietherate of triphenylmethyl lithium [1]. Later, B. M. Mikhailov and co-workers described several etherates [2] and dioxanates [3] of ArLi , even allowing for a number of errors and contradictions.** Wittig and co-workers [5] described an etherate of diphenyllithiumsodium $[(\text{C}_6\text{H}_5)_2\text{Li}]\text{Na}(\text{C}_2\text{H}_5)_2\text{O}$ similar to the dimeric complex of phenyllithium $[(\text{C}_6\text{H}_5)_2\text{Li}]_2$ found by us (but not isolated) in ethereal solutions. These compounds are the first members of the succeeding series of complexes: $[(\text{C}_6\text{H}_5)_2\text{Li}]_2$, $[(\text{C}_6\text{H}_5)_2\text{Se}]_2\text{Li}$, $[(\text{C}_6\text{H}_5)_2\text{S}]_2\text{Li}$, $[(\text{C}_6\text{H}_5)_2\text{Al}]_2\text{Li}$, etc., which extends into both aromatic and aliphatic compounds [6]. As shown by Wittig [6], dioxanates, for example $[(\text{C}_6\text{H}_5)_2\text{Mg}]_2\text{Li} \cdot 2\text{C}_6\text{H}_5\text{O}_2$ or $[(\text{C}_6\text{H}_5)_2\text{Cd}]_2\text{Li} \cdot 4\text{C}_6\text{H}_5\text{O}_2$, are formed by the action of dioxane on ethereal solutions of these compounds.

According to our data, the etherates of aliphatic and the simplest aromatic organolithium compounds (ethyl lithium, phenyl- and tolyllithium) are extremely soluble, even at low temperatures.

We isolated from an ethereal solution of p-tollyllithium at -70° the corresponding etherate $p\text{-CH}_3\text{C}_6\text{H}_4\text{Li} \cdot (\text{C}_2\text{H}_5)_2\text{O}$. Under these conditions, the crystals obtained from the ethereal solution of phenyllithium had an ether content which varied from 1.3 to 1.6 moles per mole of $\text{C}_6\text{H}_5\text{Li}$, the variation being connected, apparently, with the difficulty in drying the crystals at the low temperature. We failed to isolate the etherate of phenyllithium in an individual form. At -75° , a solution of 3.5 g of pure ethyllithium in 15 ml of ether congealed into a compact waxy mass which dissolved on an increase in the temperature or on dilution.

The difficulty in isolating pure organometallic compounds ($\text{C}_6\text{H}_5\text{Li}$, $\text{CH}_3\text{C}_6\text{H}_4\text{Li}$) or their etherates from ethereal solutions may be the formation of complexes with inorganic salts (LiBr , LiI , etc.). It is probable that this same thing makes it difficult to isolate pure diphenylberyllium from the usual reaction mixtures [6]. The effect of the nature of the radical is seen, for example, in the etherate of α -naphthyllithium, which easily crystallizes in the presence of an excess of the etherate of lithium bromide and can be obtained in the pure form by the usual reaction of phenyllithium with α -bromonaphthalene at -25° (cf. [2]).

We carried out the preparation of pure dioxanates of organolithium compounds by the usual route — the addition of dioxane, until precipitation ceased, to a solution of pure (free from halide salts) organolithium compounds** in ether with cooling. The dioxanates isolated by us contained 1 mole of dioxane per mole of organolithium compound. The dioxanate of ethyllithium, isolated for the first time, is of particular interest. In order to more completely confirm the structure of the dioxanates obtained, in addition to analysis for

* 1,4 Dioxane throughout the article.

** The incorrect interpretation by them of the ternary phenyllithium complex $2\text{C}_6\text{H}_5\text{Li} \cdot \text{LiBr} \cdot 2\text{C}_2\text{H}_5\text{O}$ as the etherate of phenyllithium has been noted by us previously [4].

*** It is not clear why, using the method developed by us for the isolation of individual organolithium compounds from the corresponding R_3Sb in benzene medium, B. M. Mikhailov and P. M. Aronovich [12] found it more convenient to refer to the work of Gilman and Woods, who never prepared nor described individual ArLi by such a route [13].

lithium, we determined the dioxane content by complexing it with lithium bromide, according to a method developed by us.

In attempting to prepare, by the method of B. M. Mikhailov and N. G. Chernova [3], dioxanates of organolithium compounds, $ArLi \cdot 2C_4H_9O_2$, described by them, we were led to the unexpected conclusion that the results and analyses presented in this work are totally non-reproducible. Under the conditions described by B. M. Mikhailov and N. G. Chernova, by the action of a solution of aryl bromide in excess dioxane on a 2 N solution of n-butyllithium in benzene, with vigorous evolution of heat, precipitates were, indeed, formed, but these precipitates were, by no means, the dioxanates described by the cited authors, but were mixtures comprising chiefly the dioxanate of lithium bromide. In the case of the "dioxanate" of phenyllithium, the lithium bromide content of the precipitate was 30-35%, and for the "dioxanates" of α -naphthyllithium and p-tolylithium it was 28 and 42% respectively.*

Moreover, we may also note that, in the action of an excess of dioxane on a suspension of p-tolylithium in benzene, i.e., under the same conditions but using a well-known $ArLi$, the dioxanate formed goes into solution without noticeable heat evolution (a precipitate is not formed). The vigorous evolution of heat observed by Mikhailov and Chernova does not pertain to the formation of a dioxanate, but is the result of the reaction of n-butyllithium with dioxane (cf. [7]).

It is also interesting to note that the action of dioxane on an ethereal solution of the ternary complexes $2RLi \cdot LiBr \cdot 2(C_2H_5)_2O$, where R is phenyl or p-tolyl [4], results in the formation of precipitates in which the ratio $RLi : LiBr : C_4H_9O_2$ is 2:1:3. These precipitates are probably mixtures of the above-described dioxanates of RLi and the dioxanates of lithium bromide.**

EXPERIMENTAL

All operations were carried out in an atmosphere of pure nitrogen, in a special apparatus [9], and with dry, pure solvents and materials [4].

Etherate of p-tolylithium, $p-CH_3C_6H_4Li \cdot (C_2H_5)_2O$. 3.8 g of p-tolylithium in 25 ml of absolute ether was cooled to -70° . The precipitate was filtered by suction at this same temperature, washed twice with ether (-70°), and dried in a stream of nitrogen with gradually increasing temperature to -30° until the particles of precipitate no longer stuck together. The weight was 3.15 g; the analysis is reported in Table 1, A.

Etherate of α -naphthyllithium, $\alpha-C_{10}H_7Li \cdot (C_2H_5)_2O$. To 1.8 g (0.05 mole) of ethyllithium [9] in 30 ml of ether at -30° was slowly added dropwise a solution of 10.3 g (0.05 mole) of α -bromonaphthalene in 50 ml of ether cooled to -15° ; the mixture stood for 15 minutes with cooling; the precipitate was suction filtered, washed twice with ether cooled to -15° , and dried in a stream of nitrogen. The weight was 5.9 g; the analysis is reported in Table 1, B (cf. [2]).

Dioxanate of ethyllithium, $C_2H_5Li \cdot C_4H_9O_2$. To 3.2 g of ethyllithium [4] in 40 ml of absolute ether was added dropwise 5 ml of dioxane at 0° . The snow-white precipitate of dioxanate was suction-filtered, washed 3 times with cold ether, and dried in a stream of nitrogen at room temperature for 1 hour. Weight, 3.82 g; the analysis is reported in Table 1, C. The precipitate charred in a mixture of air and nitrogen, and exploded in air.

Dioxanate of p-tolylithium, $p-CH_3C_6H_4Li \cdot C_4H_9O_2$. To 3.8 g of p-tolylithium [9] in 25 ml of absolute ether at 0° was added gradually 3 ml of dioxane in 10 ml of absolute ether. After 1 hour, the precipitate was suction filtered (see above for treatment). Weight, 2.5 g; the analysis is reported in Table 1, D.

* After the present article had been prepared for publication, there appeared an article by N. G. Chernova and B. M. Mikhailov [11], who, using a method which excluded the formation of lithium bromide during the reaction, arrived at the correct conclusion as to the composition of dioxanates RLi ; however, they did not renounce the previously described "bisdioxanates" [3], treating them now as complexes of RLi with dioxane and benzene, which is not the case.

** For a similar action of dioxane on $(C_2H_5)_2MgBr \cdot 3(C_2H_5)_2O$ with the liberation of insoluble $MgBr_2 \cdot 2C_4H_9O_2$ and dioxane-soluble $(C_2H_5)_2Mg \cdot C_4H_9O_2$ see [8].

Determination of dioxane: from 0.8 g of the dioxanate was obtained 0.71 g of $\text{LiBr} \cdot \text{C}_4\text{H}_8\text{O}_2$. The ratio of RLi to dioxane was 1:0.92.

Dioxanate of α -naphthyllithium, $\alpha\text{-C}_{10}\text{H}_7\text{Li} \cdot \text{C}_4\text{H}_8\text{O}_2$. 3.2 g of the etherate of α -naphthyllithium (see above) was dissolved in 70 ml of ether and 5 ml of dioxane in 15 ml of ether was added at $+10^\circ$. After 20 minutes, the precipitate was suction filtered (see above for treatment). Weight, 3.15 g; the analysis is reported in Table 1, E. Determination of dioxane: from 2.0 g of complex was obtained 1.46 g of $\text{LiBr} \cdot \text{C}_4\text{H}_8\text{O}_2$. The ratio of RLi to dioxane was 1:0.92 (cf. [11]).

TABLE 1

Experiment	Complex g	H_2SO_4 0.1 N	Li, %	RLi, %	Ether or dioxanate % (by dif- ference)	Equivalents		
						RLi	Ether or dioxane ...	LiBr
A	0.2515	14.50	4.60	56.49	43.51	1	1.01	none
A	0.2442	14.30	4.97	57.63	42.63	1	0.98	•
B	0.2751	13.15	3.32	64.01	35.99	1	1.01	•
B	0.2150	10.25	3.31	63.84	36.17	1	1.02	•
C	0.2247	17.45	5.39	27.91	72.09	1	1.05	•
C	0.1990	15.30	5.33	27.64	72.36	1	1.08	•
D	0.2631	13.10	3.46	48.79	51.21	1	1.16	•
D	0.2841	14.25	3.53	48.80	51.20	1	1.16	•
E	0.2890	13.30	3.19	61.62	38.38	1	0.95	•
E	0.2158	9.93	3.19	61.61	38.39	1	0.95	•
F*	0.2636	9.95	2.61	31.68	51.03	2	3.08	1.05
F	0.1768	6.15	2.49	30.23	52.73	2	3.32	1.08
G**	0.3538	12.21	2.39	33.79	48.54	2	3.18	1.18
G**	0.2729	9.85	2.50	35.36	46.82	2	2.94	1.13

* AgNO_3 0.1 N 5.25 and 3.35 ml; LiBr, %: 17.29 and 17.04.

** AgNO_3 0.1 N 7.20 and 5.60 ml; LiBr, %: 17.67 and 17.82.

*** Dioxane determined as $\text{LiBr} \cdot \text{C}_4\text{H}_8\text{O}_2$, see Text.

Dioxanate of lithium bromide, $\text{LiBr} \cdot \text{C}_4\text{H}_8\text{O}_2$. Using an ethereal solution of lithium bromide, we quantitatively precipitated dioxane, as the dioxanate of lithium bromide, from ethereal solutions or from mixtures of ether and bromobenzene (1:1). The precipitate was washed with absolute ether (2-3 times) and dried in a stream of nitrogen or dry air. The analysis for bromine was carried out by means of 0.1 N AgNO_3 .

Found %: Br 45.85; 45.79

$\text{LiBr} \cdot \text{C}_4\text{H}_8\text{O}_2$. Calculated %: Br 45.71.

Determination of dioxane in dioxanates RLi. 1-2 g of the complex was mixed with 15-20 ml of pure bromobenzene, the mixture was gradually distilled in a small column to 154° , and the distillate was collected in 15-20 ml of absolute ether. The dioxane was precipitated with a small excess of an ethereal solution of lithium bromide [4]; separation and analysis was carried out as above. The apparatus must be protected from atmospheric moisture.

Dioxane and ternary complexes $2\text{ArLi} \cdot \text{LiBr} \cdot 2(\text{C}_2\text{H}_5)_2\text{O}$ [4]. Precipitates were formed by the action of 10 ml of dioxane on ethereal solutions (5 g in 30 ml) of the ternary complexes of phenyl- and p-tolyl lithium at 10° ; the precipitates were filtered, washed 3 times with ether, and dried (2.1 and 6.8 g). According to the analytical data, the components were present in the ratio $\text{ArLi} : \text{LiBr} : \text{C}_4\text{H}_8\text{O}_2 = 2:1:3$. The analyses are reported in Table 1, F and G. Determination of the dioxane as $\text{LiBr} \cdot \text{C}_4\text{H}_8\text{O}_2$ gave 3 moles of $\text{C}_4\text{H}_8\text{O}_2$ in both cases.

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CATALYTIC ALKYLATION OF n-HEPTANE WITH PROPYLENE AND n-BUTANE WITH BUTYLENE AT HIGH TEMPERATURES AND PRESSURES

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It has previously been shown that the saturated hydrocarbons propane, n-butane [1], and n-pentane [2] react with propylene at high pressures (>300 atm.) and elevated temperatures (> 400°) to form a complex mixture of hydrocarbons. Undoubtedly, one of the principal reactions in this process is alkylation of paraffins by the olefins.

The present work had as its aim the investigation of the possibility of alkylating hydrocarbons with a greater number of carbon atoms: n-heptane and n-butene.

The reaction was carried out in a flow-type apparatus. The catalyst used consisted of aluminum oxide which had been treated with an aqueous solution of potassium bifluoride (10% by weight of the Al_2O_3) and a dilute solution of sulfuric acid and then washed with water. A detailed description of the apparatus, procedure, and catalyst preparation is given in [1].

Alkylation of n-heptane with propylene. The alkylation of alkanes from butane to dodecane with olefins under static conditions in the presence of aluminum chloride at 25-40° and 1-15 atm. pressure was studied by Ipatieff and co-workers [3]. However, experimental data were presented only on the alkylation of isobutane and n-hexane with ethylene.

K. P. Lavrovsky and A. A. Mikhnovskaya [4] alkylated n-heptane with propylene at 400° and 30 atm. in the presence of silica-alumina catalyst. The experimental data were not presented by the authors, it being stated only that the liquid products contained almost no unsaturates.

We studied the alkylation process in a flow-type system under high pressure and in the presence of a solid catalyst. Commercial n-heptane, purified by treatment with concentrated sulfuric acid and subsequent washing with a solution of soda and water, was used. After drying, the n-heptane was additionally purified by passage over silica gel, after which it had a b.p. of 97-98° and n_D^{20} 1.3300.

TABLE 1

Experiment No.	Temp., °C	Press., atm.	Wt. ratio, heptane/propylene	Space rate	Properties of liquid products by fractions									
					75°		75-100°		100-150°		150-175°		Residue	
					Vol. % in alkylate	Bromine No.	Vol. % in alkylate	Bromine No.	Vol. % in alkylate	Bromine No.	Vol. % in alkylate	Bromine No.	Vol. % in alkylate	
1	450	500	3.1	1.1	19.0	49	12.7	43	10.0	27	27.6	27	30.0	
2	450	500	1.4	3.2	17.1	—	8.5	34	14.6	50	16.8	27	43.6	
3	450	500	4.3	3.1	13.0	—	12.6	22	8.7	51	21.7	33	43.5	

The propylene was obtained by dehydration of isopropyl alcohol over aluminum oxide. The experimental conditions and results are presented in Table 1. The experiments were carried out at 450° and 500 atm. The

ratio of heptane to propylene varied in the range 1.4-4.3. The space rate of the liquid mixture is expressed in terms of liters per liter of catalyst per hour.

The catalyzate obtained was subjected to rectification in a column of 28 theoretical plates. Unsaturation in the various fractions was determined by bromine titration, and the indices of refraction were also determined. The decane fraction was subjected to chromatographic separation over silica gel.

From Table 1, it is seen that the expected decane fraction 150-175° was larger than any other fraction (heptane, octane, or nonane). It comprised 22-28 vol. % of the catalyzate. Its bromine number was lower than the bromine numbers of the other fractions. As seen from the catalyzate distillation curve for Experiment 1 (Figure 1), the bulk of the decane fraction (~ 65 %) boiled in the range 163-169°. After removal of the unsaturates by passage through silica gel, this fraction had the constants n_D^{20} 1.4145 and d_4^{20} 0.7391.

Determination of the degree of branching by infrared spectra [5] showed that this fraction consisted mainly of a mono-substituted decane - a methylnonane. Since in the Raman spectrum of this fraction the 954 cm^{-1}

frequency, which is characteristic of branching at the end of the chain [6], is missing, the methyl group is not in the 2-position.

According to the observations of Yu. P. Egorov, if the CH_3 group in singly branched alkanes (C_9 and higher) is in the 3-position, the intensity of the 2856 cm^{-1} frequency in the Raman spectrum is equal to or greater than the intensity of the 2875 cm^{-1} frequency. In our case, the intensity was lower; i.e., the methyl group was not in the 3-position. Thus, it could occupy only the 4- or 5-position.

By analogy with previously obtained results [1,2], it can be assumed that in this case also the propylene alkylated the n-heptane at a carbon atom in the 2-position giving a slightly branched hydrocarbon.

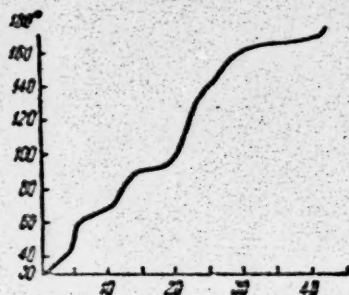
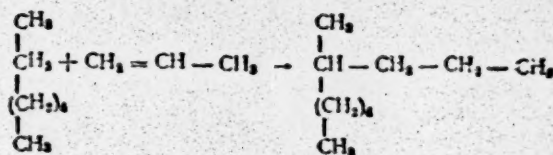


Fig. 1



The properties of the hydrocarbon isolated by us were, in fact, close to the properties of 4-methylnonane, for which [7] gives the constants: b.p. 165.7°; n_D^{20} 1.4123 and d_4^{20} 0.7323. The decane fraction also contained 7 vol. % of aromatic hydrocarbons, which were separated chromatographically over silica gel.

In Experiment 2, with 42% propylene in the initial mixture, the catalyzate obtained had a primarily saturated nature (bromine number 40). 81% of the catalyzate boiled up to 250°. The total yield of condensate at a space rate of 1.1 was 127% based on the propylene used (Experiment 1). From literature data, it is seen that n-heptane is severely cracked under static conditions, even at 400° and atmospheric pressure [8]. However, with an increase in pressure from 620 to 1860 atm., cracking decreases [9]. On the other hand, under flow conditions at normal pressure, 500°, and in the presence of zirconia-alumina catalyst, there is almost no cracking of n-heptane [10]. On passage of only n-heptane over the catalyst at 450° and 500 atm., 95% of the heptane was recovered unchanged. Only 5% of the heptane was converted into hydrocarbons boiling lower or higher than n-heptane. About 1% of the heptane was converted into gaseous products. The liquid hydrocarbons formed from the mixture of n-heptane and propylene was 6-7 times greater (38% of the heptane fed).

It should be noted that all 4 experiments were carried out using the same catalyst charge, which thus was used about 8 hours without regeneration.

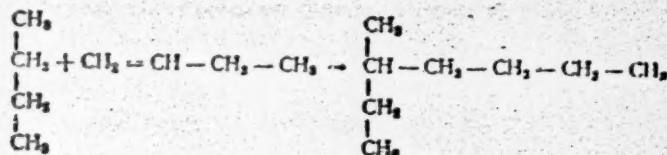
Alkylation of *n*-butane with butene. The experiments were carried out with mixtures containing 16-18% butene at pressures of 500 to 1500 atm., temperatures in the range 420-480°, and space rates of 3-6. Purities of the butene and butane were, respectively, 95 and 97%.

TABLE 2

Experiment No.	Temp., °C	Press., atm.	Wt. ratio, butene/butane	Space rate	Properties of liquid products by fractions				
					50-100°		100-125°		vol. % in catalyze
					vol. % in catalyze	bromine No.	vol. % in catalyze	bromine No.	
4	460	500	5.2	5.7	14.8	90	37.3	27	47.7
5	450	1000	5.2	3.3	14.7	63	42.0	38	43.0
6	440	1500	5.2	3.2	12.0	72	31.0	50	56.0
7	480	500	4.5	4.2	16.7	—	32.6	57	50.5
8	425	500	4.5	3.6	8.0	—	37.3	98	54.5
9	465	500	—	8.4	16.0	57	21.4	60	62.4
10	245	500	—	5.3	12.2	93	28.6	160	58.0

From Table 2, it is seen that the expected octane fraction comprised 37-42% of the catalyze. 59 ml of this fraction was subjected to rectification in a column of 47 theoretical plates. A narrow fraction, 117-119°, was collected, from which, after passage over silica gel, was obtained about 20 ml of a saturated hydrocarbon with n_D^{20} 1.4012 and d_4^{20} 0.7158.

By comparison of Raman spectra at frequencies, in cm^{-1} , of 762, 820, 874, 825, 1040, 1064, 1147, 1167, and 1302 with the catalog of spectra, it was established that the given fraction comprised chiefly 3-methylheptane. Consequently, butene alkylation of butane occurs at a secondary carbon atom.



whence, the butene reacts chiefly in the form of the α -isomer.

From Experiments 4-6, it is seen that the unsaturate content of the catalyze and that portion of the catalyze boiling above 125° increased with an increase in pressure from 500 to 1500 atm. A decrease in temperature to 425° (Experiment 8) led to a slowing down of the alkylation reaction and a marked increase in the yield of polymerization products (the bromine number of the octane fraction was 98 in this experiment).

In order to investigate the behavior of butene alone under reaction conditions, experiments were carried out with butene at 245 and 465° and a pressure of 500 atm. A highly unsaturated catalyze — the product of the polymerization of butene — was obtained in the experiment at 245°; the extent of conversion of butene into liquid products did not exceed 8%. At 465° (Experiment 9), the extent of conversion of butene into liquid products reached 50%. Upon fractionation of this catalyze in a column of 28 theoretical plates, there was obtained an octane fraction (100-125°), in the amount of 21.4 vol. %, with a bromine number of 60, which indicates an appreciable content of unsaturated hydrocarbons.

Fig. 2 shows the great similarity of the distillation curves of the catalyzes obtained in Experiments 4 and 9. In particular, the formation of a narrow fraction boiling at 117-119° is observed in both cases. Apparently, 3-methylheptane was also formed in Experiment 9.

It has been shown that 3-methylheptane can also be a product of another reaction — redistribution of hydrogen

in 1-octene (at 450° in the presence of silica-alumina catalyst). Since, in Experiment 9 with n-butene alone, the increase in catalyst weight due to carbon formation was 25% after 30 minutes, it can be assumed that saturation of the catalyzate was due to a hydrogen-transfer reaction. In Experiment 4, carbon on the catalyst after 3 hours was only 6%; in this case, hydrogen transfer must not have played a large part. Considering also that the yield of octane fraction in Experiments 4-7 (alkylation of butane with butene) was 1.5-2 times higher than in Experiment 9, and that the unsaturates were 2 times lower, it can be stated with assurance that the catalyzate obtained from the n-butane-butene mixture was mainly an alkylation product.

The results of our work show that, not only the lower, gaseous hydrocarbons, but also liquid, normal hydrocarbons can be alkylated with olefins. Therefore, it can be assumed that the primary alkylation product formed in the process can undergo further alkylation by olefins. This is one of the reasons for the complex nature of the alkylate.

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CONTACT TRANSFORMATIONS OF 1,1'-DIMETHYLDICYCLOHEXYL IN THE PRESENCE OF PLATINIZED CARBON

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and Academician B. A. Kazansky

In the investigations of B. A. Kazansky and A. L. Liberman on the contact transformations of 1,1-dimethylcyclohexane in the presence of platinized carbon, it was shown that platinized carbon catalyzes the conversion of this hydrocarbon into toluene, which is then partially methylated forming ortho- and meta-xylene [1].

Under the conditions of the experiments, other 1-methyl-1-alkylcyclohexanes undergo similar conversions. Thus, for example, we established that in presence of platinized carbon and at a temperature of 320° 1-methyl-1-ethyl-, 1-methyl-1-propyl-, and 1-methyl-1-butylcyclohexane are dehydrogenated with the formation of toluene and the corresponding monoalkylbenzenes, the toluene being partially methylated to ortho- and meta-xylenes [2].

In comparing the behavior of the 1-methyl-1-alkylcyclohexanes in the presence of a dehydrogenation catalyst, it should be noted that the relative stability of the molecule of original hydrocarbon toward contact transformation under the conditions of our experiments increases with an increase in the number of carbon atoms in the alkyl radical. During dehydrogenation of 1-methyl-1-alkylcyclohexanes, it is the methyl group which is preferentially split off, and not the other alkyl group, and this, all things considered, is what leads to the decreased yield of toluene in comparison with the corresponding alkylbenzene.

It appeared to us to be of interest to study the behavior of 1,1'-dimethyldicyclohexyl in the presence of a dehydrogenation catalyst, this being a hydrocarbon of symmetrical structure with two quaternary carbon atoms and two six-membered rings connected together in the molecule.

1,1'-dimethyldicyclohexyl, which was synthesized by us, was contacted at 320° with 10% platinized carbon. Using silica gel chromatography, fractionation, and fractional crystallization, we isolated from the catalyzate toluene, fluorene, 1-methyl-1-phenylcyclohexane, ortho-tolylbenzene, diphenyl, and 1-methyl-1-cyclohexylcyclohexane.

The approximate percentage hydrocarbon content of the catalyzate was as follows: toluene, about 70%; fluorene, about 14%; ortho-tolylbenzene, about 4%; 1-methyl-1-phenylcyclohexane, about 4%; diphenyl, about 6%; 1-methyl-1-cyclohexylcyclohexane, about 2%.

The considerable amount of toluene in the products of the catalysis indicates that, along with dehydrogenation, cleavage of the molecule at the 1,1'-carbon-carbon bond (the bond between the rings) is fundamental.

This phenomenon is in contradiction to the previous observations, according to which the methyl group in gem-methylalkylcyclohexanes is preferentially split off in the presence of a dehydrogenation catalyst, and the tendency toward splitting off of the alkyl group decreases with an increase in the number of carbon atoms. Apparently, this non-conformity can be explained by the emergence, during catalytic dehydrogenation of 1,1'-dimethyldicyclohexyl, of forces in both six-membered rings, as a result of the interaction of the hydrocarbon molecule with the catalyst, which forces are directed toward the loosening and rupture of the carbon-carbon bond common to these rings, and this, in the final analysis, leads to the formation of toluene as the chief product of the catalysis.

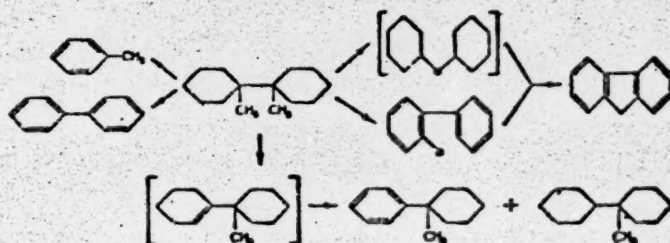
However, the presence in the products of the catalysis of small amounts of diphenyl, 1-methyl-1-phenylcyclohexane, and 1-methyl-1-cyclohexylcyclohexane indicates that, during catalytic transformations of 1,1'-dimethyldicyclohexyl, one or two methyl groups are also split from its molecule, although to a small extent.

The presence of fluorene in the catalyzate attests to the following series of reactions, along with the above-indicated types of reactions, during contacting of 1,1'-dimethyldicyclohexyl with platinized carbon: splitting off of one of the methyl groups and dehydrogenation of the six-membered ring takes place; then the other methyl group migrates into the ortho-position, and, simultaneously with dehydrogenation of the second six-membered ring, the resulting ortho-tolylbenzene undergoes closure of a new five-membered ring which results in the formation of fluorene.

Literature data confirm the possibility of the formation of fluorene under conditions of catalytic dehydrogenation [3].

Apparently, it can be assumed that the 1-methyl-1-phenylcyclohexane and 1-methyl-1-cyclohexylcyclohexane in the catalyzate is formed as follows: first, one of the gem-methyl groups is split off forming methane and 1-methyl-1-cyclohexenylcyclohexane, which then undergoes further transformation in two directions. First, there occurs further dehydrogenation of the six-membered ring which has no gem-methyl group, thereby forming 1-methyl-1-phenylcyclohexane; second, the 1-methyl-1-cyclohexenylcyclohexane undergoes the "irreversible catalysis" of N. D. Zelinsky, resulting in the formation of 1-methyl-1-cyclohexylcyclohexane and, again, 1-methyl-1-phenylcyclohexane.

The experimental material obtained permits the presentation of the following possible scheme of the transformations of 1,1'-dimethyldicyclohexyl during contacting with platinized carbon at 320°.



Synthesis of 1,1'-dimethyldicyclohexyl. A Grignard reaction of cyclohexanone with methylmagnesium iodide gave 1-methyl-1-cyclohexanol which, by agitation in the cold with hydrochloric acid, was converted to 1-chloro-1-methylcyclohexane. This chloride was converted to a Grignard reagent by the reaction with magnesium in ethereal medium; a molar quantity of an ethereal solution of 1-chloro-1-methylcyclohexane was then added, and, in addition, copper turnings and carefully dried cuprous chloride were added to the mixture as a catalyst. The reaction mixture was heated at the boiling point of ether for two days, the bulk of the ether was distilled off, dry toluene was added to the reaction flask, and the mixture was heated at the boiling point of toluene for 8 hours. After decomposition of the reaction mixture and distillation of the ether and toluene, the residue was boiled with metallic sodium and fractionated. In order to remove unsaturated hydrocarbon impurities, the 1,1'-dimethyldicyclohexyl was subjected to chromatographic adsorption on silica gel, and then again distilled under vacuum. The 1,1'-dimethyldicyclohexyl was obtained in a yield of 15.2% of theoretical. B.p. 99.5-100° (5 mm); n_D^{20} 1.4920, d_4^{20} 0.9045 M_R^{20} 62.32. Calculated for $C_{14}H_{28}$ M_R^{20} 62.45.

Found %: C 86.54, 86.67; H 13.31, 13.35
 $C_{14}H_{28}$ Calculated %: C 86.51; H 13.49.

1,1'-Dimethyldicyclohexyl has not been described in the literature.

Catalytic transformations of 1,1'-dimethyldicyclohexyl. 60 ml of 10% platinized carbon was charged

to the catalyst tube, and 32.2 g of 1,1'-dimethyl-1-cyclohexyl was passed (without a carrier gas) over the catalyst at 320° and a space rate of 0.2. The experimental results are presented in Table 1. The results of the analysis of the gas were: H_2 90.8%; CH_4 8.9%.

TABLE 1

Pass	n_D^{20} of cataly- zate	Gas evolved, ml	Catalyzate, g
1	1.5175	18945	24.9
2	1.5200	7835	22.6
3	1.5247	950	21.2
Total		27760	

TABLE 2

Fraction No.	Boiling range, °C at 5 mm	n_D^{20}	d_4^{20}	Weight, g
1	90-95°	1.5228	0.9392	0.90
2	95-110°	1.5625	—	0.20
3	110-115°	1.5689	0.9973	0.85
4	115-145°	Crystals	—	1.45
	Residue and loss			0.30

Upon fractionation of the liquid part of the catalyzate, 14.5 g of hydrocarbon with a b.p. of 103-111° (756 mm), n_D^{20} 1.4967, d_4^{20} 0.8665 was obtained. Comparison of the constants of this fraction with the literature data for toluene showed that it consisted of toluene. Nitration of this fraction gave a product which melted at 69°. A mixed melting point determination of the sample with 2,4-dinitro-toluene gave no depression of the melting point.

The part of the catalyzate remaining after separation of the toluene (6.6 g) was subjected to chromatographic adsorption on silica gel in order to separate the naphthenic portion of the catalyzate from the aromatic hydrocarbons. From the chromatography, 0.45 g of naphthenic hydrocarbons was obtained with a b.p. 103-105° (9 mm) and n_D^{20} 1.4815.

Judging by its constants, this hydrocarbon was identical with 1-methyl-1-cyclohexylcyclohexane specially synthesized by us, which was prepared by hydrogenation of 1-methyl-1-phenylcyclohexane and which had a b.p. of 104.5-105° (9 mm), n_D^{20} 1.4824, d_4^{20} 0.8897.

The aromatic portion of the catalyzate (6.0 g), obtained during the silica gel chromatography, was subjected to cooling by dry ice-acetone mixture in order to separate crystalline hydrocarbons formed during the catalysis. As a result of this freezing technique, 2.30 g of crystals were obtained, which, after recrystallization from alcohol, melted at the melting point of fluorene, 114° [4]. A mixed melting point of these crystals with pure fluorene gave no depression of the melting point.

The non-crystallizing portion of the catalyzate (3.7 g) was fractionated under vacuum. The results of the distillation are presented in Table 2.

The first fraction (b.p. 90-95° (5 mm)), according to its constants, corresponded to 1-methyl-1-phenylcyclohexane, for which N. G. Sidorova [5] gives b.p. 93° (5 mm), n_D^{20} 1.5210, d_4^{20} 0.9392.

The second fraction (b.p. 110-115° (5 mm)) was oxidized with potassium permanganate in order to determine quantitatively its content of aromatic hydrocarbons [6]. By oxidation of 0.8 g of the fraction, 0.3 g of an acid with m.p. of 112-114° (recrystallized from ethanol) was obtained. The constants of this acid agree well with the literature data for ortho-phenylbenzoic acid, for which is given a m.p. of 113.5-114.5° [7].

Oxidation results provide a basis for presuming that the third fraction comprised chiefly ortho-tolylbenzene.

From the fourth fraction (b.p. 115-145° (5 mm)), by fractional crystallization from aqueous alcohol solution, was obtained 0.8 g of diphenyl, with a m.p. of 69°, and 0.2 g of fluorene, m.p. 113-114°.

A mixed melting point determination of this diphenyl with pure diphenyl gave no depression of the melting point.

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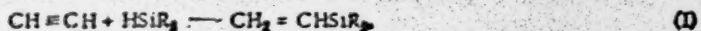
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INVESTIGATIONS IN THE FIELD OF THE SYNTHESIS AND TRANSFORMATIONS OF VINYL SILICON COMPOUNDS. SYNTHESIS OF VINYLALKYLDICHLOROSILANES BY REACTION OF ALKYLDICHLOROSILANES WITH ACETYLENE

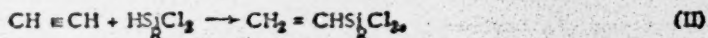
M. F. Shostakovsky and D. A. Kochkin

(Presented by Academician B. A. Kazansky, February 25, 1956)

Vinyl silicon compounds of the structure $\text{CH}_2 = \text{CHSiR}_2$, where R is halide, alkyl, or aryl, are a new class of substances and source materials for the preparation of various polymeric materials. Synthesis of these substances is based on the reaction of acetylene and hydrogen-containing alkyl- or arylsilanes or their halogen derivatives. The reaction proceeds according to

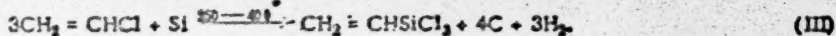


For example, we carried out the synthesis of vinylalkyldichlorosilanes using methyl- and ethyldichlorosilanes:



where R is CH_3 or C_2H_5 . These compounds can also be prepared by means of organomagnesium and organolithium compounds.

One representative of this class, vinyltrichlorosilane $\text{CH}_2 = \text{CHSiCl}_3$, was previously prepared by us by direct synthesis utilizing the reaction of vinyl chloride with an alloy of silicon and copper [1]:



A most basic and promising method for the preparation of vinyl silicon compounds is by the reaction of acetylene and the appropriate hydrogen-containing silanes (I) and (II). Considering the great reactivity of acetylene and its availability as a chemical raw material [2,3], we investigated vinylation conditions for alkyldichlorosilanes. There are not sufficient literature data on this reaction. There is a single indication by Furkhard and Krieble [5] as to the possibility of adding acetylene to a chlorosilane. There are recently published patent data indicating the possibility of reacting acetylene with certain hydrogen-containing halosilanes, using platinum on finely divided carbon [6]. However, the authors did not give yields or synthesis conditions. The reaction of methyldichlorosilane and acetylene has not been described in the literature.

In the investigation of the interaction of hydrogen-containing alkylhalosilanes with acetylene, we established that optimum results are obtained by carrying out the reaction in the presence of catalytic amounts of palladium in an autoclave at a temperature of 170-180° over a period of several hours. The alkyldichlorosilane dissolves a considerable amount of gaseous acetylene, even at room temperature. This permits charging of the required amount of acetylene and completion of the reaction with a single heating of the autoclave containing the reaction mixture. The acetylene is diluted by the vapors of the alkylhalosilane, which creates safe conditions for carrying out the reaction in the autoclave. Our experiments established that not only palladium but also nickel, boron trifluoride etherate, and platinized carbon can be used as catalysts for the vinylation reaction. When platinized carbon is used, the synthesis is carried out at higher temperatures than when palladium is used; along with this is observed very low yields of vinylalkyldihalosilanes and the formation of a large amount of tarry as well as solid, products.

Methyl- and ethyldichlorosilanes prepared by direct synthesis [8], were used as starting compounds, and these compounds are now readily accessible as synthetic raw materials. The various alkylsilanes of the structure R_nSiH_{4-n} , where R is alkyl or aryl, the various siloxanes $R_2Si-O-SiR_2$, or the silyl amine compounds

$$\begin{array}{c} H & H \\ | & | \\ R_2Si-NH-SiR_2 \end{array}$$
 i.e., compounds containing a labile hydrogen atom, certain representatives of which have

been prepared by us, can be recommended as starting compounds.

Vinylation of methyldichlorosilane in the presence of platinum on carbon. The stainless steel, 0.5-liter autoclave was charged with 90.0 g (0.78 mole) of methyldichlorosilane (b.p. 40-42°, d_4^{25} 1.1047, Cl content 61.28%) and 0.3 g of pulverized carbon containing 4.0% Pt (0.013 g Pt). Acetylene was then introduced; the autoclave was rotated 10-15 minutes, and acetylene was again introduced. The autoclave was again rotated for 40-50 minutes, and again acetylene was introduced. Owing to the high solubility of acetylene in methyldichlorosilane, it was possible to introduce 20-30 liters of gaseous acetylene. The rotating autoclave was heated to a temperature of 180-200° over a period of several hours, after which it was left overnight. As reaction was initiated, a considerable pressure decrease was registered in the autoclave.

After cooling, the reactor contents were discharged, and the reaction products were fractionated in a column of 15-20 theoretical plates, first at atmospheric pressure and then under vacuum. The following fractions were collected: 1) 40-43° (742 mm), 30.2 g; 2) 43-82° (742 mm), 2.5 g; 3) 82-91° (742 mm), 0.6 g; 4) 91° (742 mm), 2.8 g; 5) 48-82° (15 mm), 2.4 g; 6) high-boiling residue, 14.6 g. The fraction boiling at 40-43° was unreacted methyldichlorosilane. The fraction boiling at 91° at 742 mm (n_D^{25} 1.4270; d_4^{25} 1.0868; MR_D calculated for $C_3H_5SiCl_2$, 33.70; MR_D found, 33.33) contained methylvinyl-dichlorosilane $CH_3CH_2 = CHSiCl_2$ (3.2% yield based on reacted methyldichlorosilane).

Found %: C 24.90, 24.99; H 3.94, 3.91; Si 20.24, 20.20; Cl 49.74, 49.85
 $C_3H_5SiCl_2$. Calculated %: C 25.53; H 4.27; Si 19.89; Cl 50.26

Literature data for $CH_3CH_2 = CHSiCl_2$: b.p. 92-93°, d_4^{25} 1.085 [7].*

The high boiling products of the synthesis were lustrous, black resins, liquefiable by heat and possessing adhesive properties.

Vinylation of methyldichlorosilane in the presence of palladium on carbon. The autoclave was charged with 86.3 g (0.75 mole) of methyldichlorosilane and 0.8 g of palladium on aluminum oxide ($Pd-Al_2O_3$), 0.5% palladium (0.004 g palladium). Acetylene (27-28 liters) was then added as described above. The autoclave was heated to 170-180° over a period of several hours. Addition of acetylene began at 170°. The reaction products were a dark brown liquid with a sharp odor, from which the following fractions were obtained: 1) 40-43° (746 mm), 30.8 g; 2) 43-88° (745 mm), 4.7 g; 3) 88-92° (750 mm), 18.0 g; 4) 32-84° (6-11 mm), 10.0 g; 5) high boiling residue. The first fraction was original methyldichlorosilane.

The third fraction, b.p. 88-92° (750 mm), 18.0 g (n_D^{25} 1.4270, d_4^{25} 1.0870) was methylvinyl-dichlorosilane (23.0% of theoretical). The fraction boiling at 32-84° (6-11 mm) contained, apparently, products of the addition of acetylene to methyldichlorosilane of various degrees of unsaturation.

Vinylation of ethyldichlorosilane in the presence of platinum on carbon. Vinylation of 90 g (0.7 mole) of ethyldichlorosilane (b.p. 74.5° at 752 mm, n_D^{25} 1.4129, d_4^{25} 1.0849, Cl 55.0%) in the presence of 0.3 g of carbon containing 4% platinum (0.012 g of platinum) at a temperature of 180-200° over a period of several hours gave a product which was fractionated into the following fractions: 1) 70-75° (750 mm), 20.0 g; n_D^{25} 1.0845; d_4^{25} 1.0836; 2) 80-118° (750 mm), 3.0 g; 3) 118.5-119.5° (743 mm), 5.0 g; 4) 80-200° (2.5-3.0 mm), 8.0 g; 5) high-boiling residue, 22.0 g. The first fraction was unreacted ethyldichlorosilane. The third fraction, n_D^{25} 1.4385 and d_4^{25} 1.0664, contained vinyl-ethyldichlorosilane (C_4H_7) ($CH_2 = CHSiCl_2$, MR_D calculated for $C_4H_7SiCl_2$, 38.89; MR_D found 38.24).

Found %: C 30.90, 31.00; H 4.93, 5.16; Si 18.14, 18.49; Cl 45.70, 45.69.
 $C_4H_7SiCl_2$. Calculated %: C 30.98; H 5.16; Si 18.11; Cl 45.74.

Literature data for (C_4H_7) ($CH_2 = CHSiCl_2$): b.p. 122.0° (750 mm), d_4^{25} 1.053, n_D^{25} 1.4405 [6]. The yield of vinyl-ethyldichlorosilane was 3.6%. The high boiling residue, 22.0 g (16.0% yield), was a black, fusible resin which was soluble in acetone and ether.

* Purdy's preparation [7] of methylvinyl-dichlorosilane via organomagnesium synthesis from vinylsilane trichloride (b. p. 94.0-96°), separation of which from the reaction mixture is difficult owing to the closeness of boiling points is doubtful.

Vinylation of ethyldichlorosilane in the presence of platinum on carbon of low platinum content (0.004 g platinum). Upon carrying out this process in the presence of a small amount of platinum (0.004 g), even at a temperature of 230° for several hours, there was practically no vinylation; only an insignificant amount of vinylthyldichlorosilane was isolated. The major part of the ethyldichlorosilane was recovered unchanged.

Vinylation of ethyldichlorosilane in the presence of palladium on aluminum oxide (Pd - Al₂O₃). The autoclave was charged with 70.0 g of ethyldichlorosilane and 0.8 g of pulverized palladium on aluminum oxide with a palladium content of 0.5% (0.004 g of palladium). After the introduction of 37 liters of acetylene, the autoclave was heated to 160-170° over a period of several hours. Even at such a temperature, a marked pressure decrease was observed. The addition of acetylene to ethyldichlorosilane proceeded exothermically and required strict control in order to maintain the required temperature. Fractionation produced the following fractions: 1) 70-75° (750 mm), 28.0 g; 2) 94-100° (89-90 mm), 21.8 g; 3) 105° (14.5 mm), 2.4 g; n_D^{20} 1.4790; d_4^{20} 1.1870; 4) 117-121° (12-13 mm), 10.0 g; 5) 125-140° (11.5-12.0 mm), 11.9 g; 6) high-boiling residue, 2.6 g.

The first fraction, boiling at 70-75° (750 mm), was unreacted ethyldichlorosilane. From the fraction boiling at 94-100° (89-90 mm), a second fractionation isolated 19.9 g of vinylthyldichlorosilane (30.5% yield based on reacted ethyldichlorosilane). From the fraction boiling at 125-140° (11.5-12.0 mm), a second fractionation isolated a compound boiling at 140° (10.5 mm), 4.6 g; (n_D^{20} 1.4869; d_4^{20} 1.1910), apparently $C_2H_5(C_2H_5)_2SiCH_2CH=CHSi(Cl)_2C_2H_5$. MR_D found 75.05; MR_D calculated for $C_{12}H_{18}Si_2Cl_4$ 75.0.

Found %: C 30.51, 30.69; H 5.22, 5.28; Si 18.07, 18.12; Cl 44.13, 45.05.
 $C_{12}H_{18}Si_2Cl_4$ Calculated %: C 30.97; H 5.1; Si 18.1; Cl 45.70.

The high-boiling fraction, 2.6 g, was a viscous, dark colored, fusible tar.

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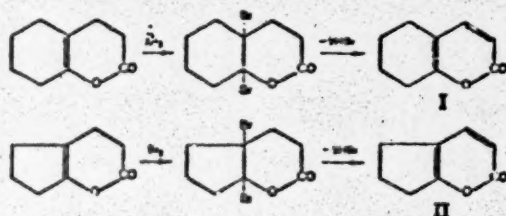
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CYANETHYLATED KETONES IN THE SYNTHESIS OF UNSATURATED δ -LACTONES. A NEW METHOD OF SYNTHESIS OF α -PYRONES

N. P. Shusherina, M. Yu. Lurye and R. Ya. Levina

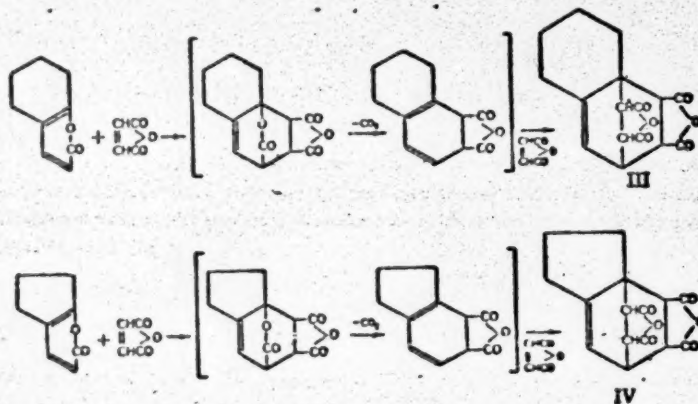
(Presented by Academician A. N. Nesmeyanov, December 19, 1955)

In our previous communications, we described the synthesis of the unsaturated δ -lactones $\Delta^{2,3}$ -hexahydrocoumarin [1,2] and 5,6-cyclopentano-3,4-dihydro- α -pyrone [2]. Bromination of these lactones was studied in the present work. It was established that on the action of bromine on unsaturated lactones with condensed rings, crystalline dibromides are formed which, on vacuum distillation in a stream of dry air readily split out two molecules of hydrogen bromide, forming the corresponding α -pyrones (I and II; 5,6-cyclohexano- α -pyrone (5,6,7,8-tetrahydrocoumarin) and 5,6-cyclopentano- α -pyrone.



Thus, bromination of unsaturated δ -lactones, in the absence of moisture, and subsequent distillation of the resulting dibromides can serve as a method for the preparation of difficultly available α -pyrones.

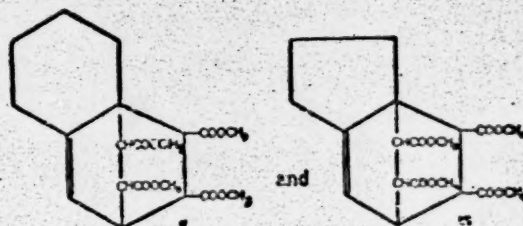
These pyrones are very stable substances which do not decolorize bromine water. Their structure was confirmed by fusion with maleic anhydride (and also by heating with maleic anhydride in toluene or xylene solution) to obtain the double addition products



(III and IV), the formation of which was attributed to the successive reactions: addition of maleic anhydride to the dienic system of the α -pyrone, splitting out of carbon dioxide from the resulting monoadduct, and addition of a second molecule of maleic anhydride.

It should be noted that the liberation of carbon dioxide in this reaction proceeds very readily, merely on heating to 100° (in toluene solution), and is concluded after only a 2-hour refluxing of the reaction mixture at this temperature. Therefore, under these conditions (fusion or heating in toluene or xylene), we were unsuccessful in isolating addition products corresponding to the addition of one molecule of maleic anhydride to the molecule of substituted α -pyrone.

This behavior of 5,6-cyclohexano- and 5,8-cyclopentano- α -pyrone in reactions with maleic anhydride differs from the behavior of other compounds of this series; α -pyrone itself (coumalin), dimethylcoumalin, the methyl ester of coumalinic acid; as shown by Diels and Alder, heating of these α -pyrones with maleic anhydride in toluene solution gives the products of a single addition, and the splitting out of carbon dioxide and the formation of products of a two-fold addition of maleic anhydride occurs only on 24-hour heating in xylene. The structures of these double addition products (III and IV) were confirmed by hydrolysis to the tetrabasic acids (basicity was determined by titration), which were further characterized as the corresponding tetramethyl esters (V and VI).



EXPERIMENTAL

5,6-Cyclohexano- α -pyrone (5,6,7,8-tetrahydrocoumarin). To a solution of 15.2 g (0.1 mole) of $\Delta^{2,3,8}$ -hexahydrocoumarin (b.p. 117-118°/5 mm; n_D^{20} 1.5050 [1,2]) in 20 ml CCl_4 was added dropwise, while cooling by ice, a solution of 16 g (0.1 mole) of bromine in 12 ml of CCl_4 . After evaporation of the CCl_4 under vacuum in a current of dry air, the residue crystallized all at once. On distillation under vacuum, vigorous splitting out of HBr occurred, and 5,6-cyclohexano- α -pyrone (12.4 g; 82.6% yield, calculated on the original lactone) readily distilled. B.p. 123-124° (4 mm); m.p. 63-64° (from alcohol).

Found %: C 72.32, 72.20; H 6.92, 7.00
 $C_9H_{10}O_2$. Calculated %: C 71.98; H 6.71.

Literature data: b.p. 115-123° at 1 mm; m.p. 64.5-65° [4].

Reaction with maleic anhydride. A mixture of 4 g (0.025 mole) of 5,6-cyclohexano- α -pyrone and 5.0 g (0.050 mole) of maleic anhydride were heated on a metal bath; vigorous evolution of carbon dioxide (passed into barium hydroxide solution) began at temperature of 150-160°, and it was concluded in 20-30 minutes. The resulting addition product (III) was recrystallized from acetone by the addition of petroleum ether (72% yield); m.p. 310-311° (sealed tube).

Found %: C 63.65, 63.60; H 4.90, 4.92
 $C_{19}H_{14}O_6$. Calculated %: C 63.90; H 4.62.

Literature data: m.p. 310-311° [4].

If the maleic anhydride is reacted with the 5,6-cyclohexano- α -pyrone in a molar ratio of 1:1, the product

of two-fold addition is still obtained, but in smaller yield. An addition product of this same composition and with the same melting point was obtained by carrying out the reaction under other conditions - by refluxing in toluene or xylene solution (at a molar ratio of cyclohexanopyrone to maleic anhydride of 1:2 and of 1:1).

Upon heating the addition product with a 20% aqueous solution of sodium hydroxide and subsequent acidification with concentrated hydrochloric acid, the crystalline acid (m.p. 306-308° in a sealed tube) was obtained, which titrated as the tetrabasic acid. The tetramethyl ester (V), m.p. 199-200° (from alcohol) was obtained by the action of an ethereal solution of diazomethane on a methanol solution of the acid.

Found %: C 61.23, 61.30; H 6.74, 6.77.
 $C_{25}H_{24}O_8$ Calculated %: C 60.91; H 6.60.

5,6-Cyclopentano- α -pyrone. To a solution of 5.2 g (0.036 mole) of 5,6-cyclopentano-3,4-dihydro- α -pyrone (b.p. 118-119° at 13 mm; n_D^{20} 1.4990 [2]) in 10 ml of ether was added dropwise 5.8 g (0.036 mole) of bromine while cooling with solid carbon dioxide. After evaporation of the ether under vacuum in a stream of dry air, white, crystalline dibromide remained in the flask. Splitting out of hydrogen bromide proceeded vigorously on heating in a vacuum, and afterwards the resulting 5,6-cyclopentano- α -pyrone was distilled (yield 1.4 g, 27.3% calculated on the basis of the original lactone): m.p. 87-88° (from aqueous alcohol).

Found %: C 70.34, 70.60; H 6.14, 6.12.
 $C_8H_6O_3$ Calculated %: C 70.62; H 5.92.

5,6-Cyclopentano- α -pyrone is not described in the literature.

Reaction with maleic anhydride. A solution of 0.9 g (0.0066 mole) of 5,6-cyclopentano- α -pyrone and 1.29 g (0.0132 mole) of maleic anhydride in 5 ml of toluene was refluxed for 2 hours; vigorous evolution of carbon dioxide (passed into barium hydroxide solution) took place. The precipitated crystals of addition product (IV) (1.6 g; 84.2% yield), after recrystallization from ethyl acetate decomposed, but did not melt, above 320°.

Found %: C 62.66, 62.38; H 4.43, 4.37.
 $C_{12}H_{12}O_6$ Calculated %: C 62.48; H 4.19.

Solution of the addition product in a 10% solution of sodium hydroxide and subsequent acidification with hydrochloric acid gave the crystalline acid, which titrated as a tetrabasic acid; treatment of its methanol solution with an ethereal solution of diazomethane gave the tetramethyl ester (VI): m.p. 203-204° (from alcohol).

Found %: C 60.00, 59.87; H 6.55, 6.56.
 $C_{18}H_{20}O_8$ Calculated %: C 60.01; H 6.36.

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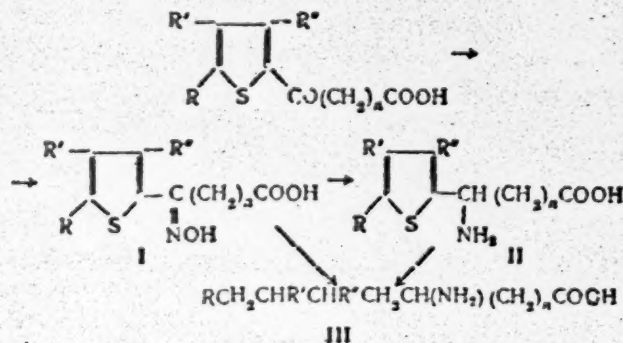
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A NEW GENERAL METHOD OF PREPARATION OF AMINO ACIDS OF THE ALIPHATIC SERIES

Ya. L. Goldfarb, B. P. Fabrichnyi and I. P. Shalavina

(Presented by Academician A. A. Balandin, February 11, 1956)

Recently, Ya. L. Goldfarb and B. P. Fabrichnyi [1] described a new method for the preparation of aliphatic α -amino acids from compounds of the thiophene series, which was based on the ability of Raney nickel to act as a desulfurizing and, in addition, a hydrogenating agent. Somewhat later it was shown by the authors, using the oxime of 2-thienylglyoxylic acid, that it is possible to arrive at aliphatic α -amino acids by Raney nickel treatment of oximino acids, which are formed by the action of hydroxylamine on the corresponding keto acids. It is entirely probable that the latter method can be extended to other oximino acids of the thiophene series. This would permit the preparation of aliphatic amino acids of different types, differing in the position of the amino group with respect to the carboxyl and having the common feature that the carbon atom bearing the amino group is joined to a chain containing not less than 4 carbon atoms:



In connection with this, it should be noted that keto acids are perfectly available compounds which are formed in yields of 60-70% by the reaction of thiophene with acyl chloride of ω -carbalkoxy acids [2]. The possibility of putting into practice this general method, which, however, must be complicated somewhat (see below), was established by us in a series of examples.

The required oximes of the keto acids were prepared in yields of 88-92% by boiling the corresponding keto acids with a large excess of hydroxylamine in aqueous alkali. As already noted above, the direct conversion of the oxime to the aliphatic amino acid was successfully accomplished only in the case of the oxime of 2-thienylglyoxylic acid. The other oximes gave oily materials under similar conditions; this required the introduction of an intermediate step: reduction of the oximes into the thiophene amino acids by the action of amalgamated aluminum, for which reduction Müller and Feld [3] recommended the substitution of water for aqueous alcohol in certain cases; this substitution leaves the yield practically unchanged, but the aluminum hydroxide filters faster. It should be noted here that this step of the process requires further study, since the product is frequently obtained in poor yield.

By the indicated route we prepared γ -(2-thienyl)- γ -aminobutyric (II, $n = 2$), δ -(2-thienyl)- δ -aminovaleric (II, $n = 3$), ϵ -(2-thienyl)- ϵ -aminocaproic (II, $n = 4$), θ -(2-thienyl)- θ -pelargonic (II, $n = 7$), and ι -(2-thienyl)-

α -aminocaproic (II, $n = 6$) acids, and by hydrogenolysis of the first four of them using skeletal nickel we prepared γ -amino-*n*-caprylic (III, $n = 2$), δ -amino-*n*-pelargonic (III, $n = 3$), ϵ -amino-*n*-capric (III, $n = 4$), and θ -amino-*n*-tridecanoic (III, $n = 7$) acids. Certain of the enumerated amino acids could not be freed of very small amounts of mineral impurities; for this reason, the deviations observed during their analysis were somewhat larger than the experimental error of the analytical method; however, analysis of the *p*-toluenesulfonic derivatives of these amino acids gave results which were in good agreement with the calculated values.

EXPERIMENTAL

Preparation of amino acids of the thiophene series. By the reaction of thiophene with acyl chlorides of the corresponding ω -carboxylic acids according to the published method [2], these keto acids were prepared: β -(2-thienyl)-propionic, γ -(2-thienyl)-butyric, δ -(2-thienyl)-valeric, η -(2-thienyl)-caprylic, and θ -(2-thienyl)-pelargonic acids. The previously known η -(2-thienyl)-caprylic acid was synthesized by us with a yield of 67% by the action of the acyl chloride of ω -carboxycaprylic acid on thiophene; its m.p. was 62-63.5° (after recrystallization from dilute alcohol).

Found %: C 61.55, 61.55; H 7.12, 7.11; S 12.29, 12.57.
 $C_{13}H_{14}O_2S$. Calculated %: C 61.39; H 7.13; S 12.60.

Oxime of β -(2-thienyl)-propionic acid (I, $n = 2$). A solution of 50.4 g of β -(2-thienyl)-propionic acid, 61 g NaOH, and 57.5 g $NH_2OH \cdot HCl$ in 550 ml water was refluxed for 4 hours. After acidification of the cooled solution with conc. HCl, an oil, which quickly crystallized, separated out. The precipitate was filtered, washed with water, and dried in a vacuum over P_2O_5 . 50.5 g of the oxime (92% yield) was obtained. After recrystallization (with activated carbon) from water, its m.p. was 135°.

Found %: C 48.35, 48.20; H 4.33, 4.30; S 15.81, 15.96; N 6.75, 6.82
 $C_9H_8O_2NS$. Calculated %: C 48.23; H 4.55; S 16.09; N 7.03.

Oxime of γ -(2-thienyl)-butyric acid (I, $n = 3$). The yield of oxime was 88.2%, m.p. 123-124° (after recrystallization from water).

Found %: N 6.46, 6.51.
 $C_9H_{10}O_2NS$. Calculated %: N 6.57.

The Oxime of δ -(2-thienyl)-valeric acid (I, $n = 4$) was obtained with a yield of 88.5%, m.p. 116.5-118° (from water).

Found %: N 6.22, 6.12.
 $C_{10}H_{12}O_2NS$. Calculated %: N 6.16.

Oxime of η -(2-thienyl)-caprylic acid (I, $n = 7$). The yield was 87%, m.p. 114.5-115° (after recrystallization from dilute alcohol).

Found %: N 5.37, 5.25.
 $C_{13}H_{16}O_2NS$. Calculated %: N 5.20.

Oxime of θ -(2-thienyl)-pelargonic acid (I, $n = 8$). The yield was 87%. After several recrystallizations from dilute alcohol and dilute dioxane, the oxime melted at 106-106.5°.

Found %: N 4.83, 4.99.
 $C_{14}H_{18}O_2NS$. Calculated %: N 4.94.

γ -(2-Thienyl)- γ -aminobutyric acid (II, $n = 2$). A mixture of amalgamated Al (obtained from 24 g of granular Al), 12 g of the oxime of β -(2-thienyl)-propionic acid, and 240 ml of water was agitated for 16 hours. The precipitate was separated and washed several times with hot water. The filtrate was evaporated to dryness under vacuum. The weight was 3.88 g (34.8% yield). After recrystallization from dilute alcohol, the m.p. was 170-171°.

* In all cases the melting point was determined in a preliminarily heated apparatus.

Found %: C 51.65, 51.94; H 6.08, 5.85; S 17.07, 17.23; N 7.65, 7.48.
 $C_8H_{11}O_2NS$. Calculated %: C 51.88 H 5.98; S 17.31 N 7.58.

The p-toluenesulfonic derivative of the amino acid melted at 131.5-132° after recrystallization from dilute alcohol.

Found %: N 4.08, 4.05.
 $C_{13}H_{17}O_4NS_2$. Calculated %: N 4.13.

δ -(2-Thienyl)- δ -aminovaleric acid (Π , $n = 3$). A solution of 11.2 g of the oxime of γ -(2-thienyl)-butyric acid in 224 ml of 50% alcohol was agitated 16 hours with amalgamated Al prepared from 22.4 g of granular Al. Further treatment was carried out as indicated above. 4.47 g of δ -(2-thienyl)- δ -aminovaleric acid (42% yield) was obtained. The m. p. was 156-157° after recrystallization from dilute alcohol.

Found %: C 54.30, 54.31; H 6.56, 6.71; N 6.83, 6.89.
 $C_9H_{11}O_2NS$. Calculated %: C 54.24; H 6.57; N 7.03.

The p-toluenesulfonic derivative of the amino acid had a m.p. of 128-129° after recrystallization from dilute alcohol.

Found %: N 3.93, 3.97.
 $C_{14}H_{19}O_4NS_2$. Calculated %: N 3.96.

ϵ -(2-Thienyl)- ϵ -aminocaproic acid (Π , $n = 4$). Amalgamated Al, prepared from 20 g of granular Al, 9.6 g of the oxime of δ -(2-thienyl)-valeric acid, and 350 ml of water were agitated 16 hours. The precipitate was separated and washed with hot water. To the filtrate, which had been evaporated under vacuum to a volume of about 400 ml, was again added amalgamated Al, prepared from 15 g of granular Al. The mixture was agitated 16 hours. Further treatment was carried out in the manner described in the preceding experiments. After driving off the water, the residue was washed with a mixture of ethyl and isopropyl alcohols. The weight of dry material was 2.54 g (28.2% yield). After repeated crystallizations of the amino acid from a mixture of ethyl and isopropyl alcohols, it melted at 166-168°.

Found %: C 55.71, 55.56; H 7.05, 7.14; N 6.32, 6.25.
 $C_{21}H_{25}O_4NS$. Calculated %: C 56.30; H 7.08 N 6.57.

The p-toluenesulfonic derivative of this amino acid had a m.p. of 81.5-83° after recrystallization from dilute alcohol.

Found %: C 55.63, 55.98; H 5.72, 5.79; N 3.63, 3.76.
 $C_{17}H_{21}O_4NS_2$. Calculated %: C 55.56; H 5.76; N 3.81.

θ -(2-Thienyl)- θ -aminopelargonic acid (Π , $n = 7$). was prepared from the oxime of η -(2-thienyl)-caprylic acid under the conditions used for the reduction of the oxime of β -(2-thienyl)-propionic acid. From 15 g of the oxime was obtained 2.96 g θ -(2-thienyl)- θ -aminopelargonic acid with a m.p. of 162-169°.

Found %: C 60.67, 60.56; H 8.19, 8.16; S 12.44, 12.56; N 4.87, 4.90.
 $C_{19}H_{23}O_2NS$. Calculated %: C 61.14. H 8.29; S 12.54; N 5.49.

The p-toluenesulfonic derivative of the amino acid melted at 114.5-115.5° after recrystallization from dilute alcohol.

Found %: C 58.41, 58.42; H 6.58, 6.75; N 3.42, 3.55.
 $C_{23}H_{27}O_4NS_2$. Calculated %: C 58.64; H 6.65; N 3.42.

ι -(2-Thienyl)- ι -capric acid (Π , $n = 8$). was prepared by reduction of θ -(2-thienyl)-pelargonic acid. The m.p. was 152-153.5° after recrystallization from dilute alcohol.

Found %: C 62.02, 62.11; H 8.39, 8.49; N 5.07, 4.98.
 $C_{21}H_{27}O_2NS$. Calculated %: C 62.41; H 8.60; N 5.20.

γ -Amino-n-caprylic acid (III, $n = 2$). 25 g of skeletal nickel was added with stirring to a solution of 5.0 g of γ -(2-thienyl)- γ -aminobutyric acid in 250 ml of water heated to 65°. Agitation at 65-70° was continued for 3 hours (to a negative qualitative reaction for S, sodium nitroprusside test). The catalyst was filtered off and repeatedly washed with hot water. The combined filtrates were evaporated to dryness under vacuum. The residue was dried in a vacuum over P_2O_5 . The weight was 3.5 g (73% yield, taking into account the water of crystallization). Purification was accomplished by boiling the solution of the amino acid with activated carbon; a 7-fold volume of alcohol was added to the filtrate. Upon cooling the solution with ice, a precipitate separated, which was filtered off and dried in a vacuum over P_2O_5 .

Found %: C 54.40, 54.31; H 10.76, 10.69; N 7.86, 7.72.
 $C_8H_{11}O_2N \cdot H_2O$. Calculated %: C 54.22; H 10.81; N 7.91.

Analytical data showed that, after drying for a day in a vacuum desiccator over P_2O_5 , the γ -aminocaprylic acid contained water of crystallization. The latter was eliminated by drying the amino acid in a vacuum over P_2O_5 for 2.5 hours at 80°. The anhydrous amino acid melted at 147-149°.

The p-toluenesulfonic derivative of the γ -aminocaprylic acid melted at 99-100° after recrystallization from dilute alcohol.

Found %: N 4.56, 4.45.
 $C_{15}H_{21}O_4NS$. Calculated %: N 4.47.

δ -Amino-n-pelargonic acid (III, $n = 3$). 2.05 g of δ -aminopelargonic acid (53% yield) was obtained by the action of 24 g of skeletal Ni on 4.45 g δ -(2-thienyl)- δ -aminovaleric acid. The amino acid was purified by reprecipitation from alcoholic solution by ether and by crystallization from isopropyl alcohol. M.p. 129-129.5°. The amino acid was readily soluble in water and ethyl alcohol.

Found %: C 62.28, 62.25; H 11.06, 11.06; N 7.77, 7.79.
 $C_9H_{13}O_2N$. Calculated %: C 62.47; H 11.07; N 8.10.

The p-toluenesulfonic derivative had a m.p. 96.5-98° after recrystallization from dilute alcohol.

Found %: N 4.22, 4.17.
 $C_{16}H_{22}O_4NS$. Calculated %: N 4.28.

ϵ -Amino-n-capric acid (III, $n = 4$). By hydrogenolysis of 4.3 g of ϵ -(2-thienyl)- ϵ -aminocaproic acid under the above-indicated conditions there was obtained 1.52 g of ϵ -aminocapric acid (40% yield). It melted at 190.5-192° after reprecipitation from alcoholic solution by ether.

Found %: C 63.46, 63.28; H 10.85, 10.80; N 7.12, 7.27.
 $C_{10}H_{17}O_2N$. Calculated %: C 64.12; H 11.30; N 7.48.

The p-toluenesulfonic derivative melted at 98-98.5° after recrystallization from dilute alcohol.

Found %: C 59.79, 59.73; H 8.03, 7.84; S 9.70, 9.64; N 3.98, 3.85.
 $C_{17}H_{27}O_4NS$. Calculated %: C 59.79; H 7.97; S 9.39; N 4.10.

θ -Amino-n-tridecanoic acid (III, $n = 7$). Hydrogenolysis of θ -(2-thienyl)- θ -aminopelargonic acid was as indicated above, but in the presence of NH_3 . 1.45 g of θ -aminotridecanoic acid was obtained from 3.4 g of the original amino acid. The amino acid was purified by recrystallization from absolute isopropyl alcohol. M.p. 127-129°.

Found %: C 67.30, 67.17; H 11.56, 11.62; N 5.90, 5.89.
 $C_{13}H_{27}O_2N$. Calculated %: C 68.06; H 11.87; N 6.11.

The p-toluenesulfonic derivative melted at 58-59° after recrystallization from dilute alcohol.

Found %: C 62.49, 62.23; H 8.40, 8.60; N 3.61, 3.68.
 $C_{20}H_{33}O_4NS$. Calculated %: C 62.63; H 8.67; N 3.65.

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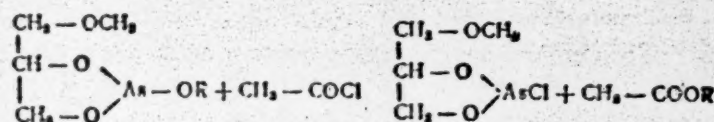
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THE ACTION OF ACYL HALIDES AND OF THE ANHYDRIDE OF ACETIC ACID ON GLYCOL ESTERS OF PHENYLARSINOUS ACID

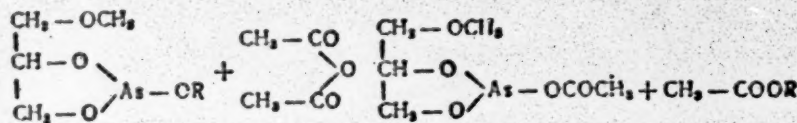
Gilm Kamal and N. A. Chadaeva

(Presented by Academician A. E. Arbuzov, January 18, 1956)

In a previous work [1], we showed that alkyl esters of α -methoxypropyleneglycolarsenous acid enter comparatively readily into a simple exchange reaction with acetyl chloride according to the equation:



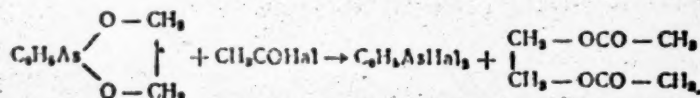
The above-indicated ester also reacts without ring cleavage on heating with acetic anhydride with the formation of the corresponding acetate and the monoacetyl derivative of α -methoxypropyleneglycolarsenous acid:



Thus, it was shown by us that mixed cyclic esters of arsenous acid react with acetyl chloride and with acetic anhydride in an exchange reaction in which the ring $\begin{array}{c} > \text{C} - \text{O} \\ | \\ > \text{C} - \text{O} \end{array} \text{As} -$ is quite stable and is retained.

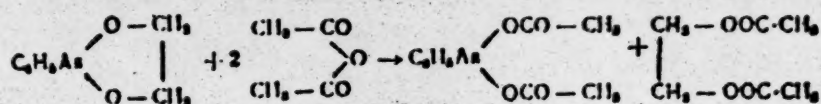
The present small work is a further development of our investigations in the field of cyclic glycol ester of arylarsinous acids and their properties. Here we have set ourselves the goal of studying the reaction of acyl halides and of the anhydride of acetic acid with cyclic esters of a phenylarsinous acid and of clarifying thereby whether the reaction proceeds with complete or partial ring cleavage.

The experiments carried out by us on the reaction of the ethylene glycol ester of phenylarsinous acid with both acetyl chloride and bromide showed that an exchange reaction occurs with the liberation of a considerable amount of heat, with the formation of ethylene glycol diacetate and of phenyldihaloarsine:

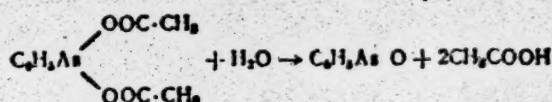


where Hal is Cl or Br.

It was also established by us that on heating a mixture of acetic anhydride and the ethylene glycol ester of phenylarsinous acid, ring cleavage occurs and two compounds are formed: ethylene glycol diacetate and the diacetyl derivative of phenylarsinous acid:



The diacetyl derivative of phenylarsinous acid is a clear, oily liquid with a sharp odor reminiscent of acetic acid. It is rapidly hydrolyzed by water.



The action of acetic anhydride on the pyrocatechol ester of phenylarsinous acid also leads to similar results; two compounds are formed: crystalline pyrocatechol diacetate and diacetoxypenylarsine.

Thus, in our synthesis of the diacetyl derivative of phenylarsinous acid a series of acetyl derivatives of arsenous acid is added:



EXPERIMENTAL

The starting materials, the ethylene glycol and the pyrocatechol esters of phenylarsinous acid, were described by us earlier [3].

The action of acetyl chloride on the ethylene glycol ester of phenylarsinous acid. Into an Arbuzov distillation flask was placed 12.3 g of ethylene glycol ester of phenylarsinous acid, and 9.1 g of acetyl chloride was added from a dropping funnel. The temperature of the reaction mixture was increased by this from 26 to 97°. The contents of the flask were further heated on an oil bath at 155° for a period of 1 hour. After cooling, a vacuum distillation was carried out. The following fractions were obtained: I, 70-81°/12 mm, 6.3 g; II, 110-114°/10 mm, 7.3 g; III, 114-115°, 1.3 g.

From Fraction I, by a second distillation, was obtained 4.1 g of a substance boiling at 186-188° with n_D^{20} 1.4203, d_4^{20} 1.0278. According to the analytical data, it was ethylene glycol diacetate. Fraction III was analyzed without further purification.

Found %: As 33.76, 33.78; Cl 31.67, 31.78.

$\text{C}_6\text{H}_5\text{AsCl}_2$. Calculated %: As 33.60; Cl 31.80.

According to analysis for arsenic and chlorine, Fraction III was pure phenyldichloroarsine.

The action of acetyl bromide on the ethylene glycol ester of phenylarsinous acid. With external cooling 13 g of acetyl bromide was added dropwise to 12.15 g of the ethylene glycol ester of phenylarsinous acid. The reaction proceeded with the liberation of a considerable amount of heat. At the conclusion of the addition, the mixture was heated on an oil bath for an hour to 100-103°. The following fractions were obtained by vacuum distillation: I, 71-78°/10 mm, 7.5 g; II, 129-138°/10 mm, 4.2 g; III, 143-144°/10 mm, 10.9 g.

After washing Fraction I with soda solution and twice with water and drying, the remaining liquid was distilled. B.p. 186-187° and n_D^{20} 1.4145. Fraction III was analyzed without additional distillation.

Found %: As 23.95, 24.02; Br 50.31; 50.92.

$C_8H_5AsBr_2$. Calculated %: As 24.02; Br 51.25.

Thus, the action of acetyl bromide on the ethylene glycol ester of phenylarsinous acid is also an exchange reaction resulting in the formation of ethylene glycol diacetate and phenyldibromoarsine.

The action of acetic anhydride on the ethylene glycol ester of phenylarsinous acid. Into a distillation flask were placed 13.15 g of the ethylene glycol ester of phenylarsinous acid and 12.7 g of acetic anhydride. The mixture was further heated on an oil bath to the boiling point of acetic anhydride for 6 hours. The following fractions were then obtained by vacuum distillation: I, 50-77°/14 mm, n_D^{20} 1.4185, 9.2 g; II, 152-168°/18 mm, n_D^{20} 1.5481, 3.15 g; III, 128-130°/2 mm, n_D^{20} 1.5485, 7.9 g.

After the corresponding treatment, ethylene glycol diacetate, b.p. 186-186°* and n_D^{20} 1.4184, was isolated from Fraction I by distillation. From Fraction III was isolated a fraction boiling at 128-129°/2 mm.

Found %: As 27.81, 27.54.

$C_{10}H_{11}AsO_4$. Calculated %: As 27.73.

According to the analytical data, the substance obtained was diacetoxypheylarsine $C_6H_5As(OCOCH_3)_2$. It was a clear liquid with d_4^{20} 1.4268 and n_D^{20} 1.5485. In moist air it quickly became covered with a white film, probably phenylarsine oxide.

The action of acetic anhydride on the pyrocatechol ester of phenylarsinous acid. In a manner analogous to that described above, a mixture of 7.8 g of the pyrocatechol ester of phenylarsinous acid and 6.0 g of acetic anhydride was heated on an oil bath for 5 hours at 120°. The following fractions were obtained by vacuum distillation: I, 117-122°/3 mm, n_D^{20} 1.5092, 3.7 g; II, 123-137°/3 mm, n_D^{20} 1.5495, 6.0 g.

Fraction I soon crystallized. The crystals were washed to neutrality with a solution of bicarbonate and then twice with hot water. After cooling, the crystals were separated, pressed between sheets of filter paper, and dried in air. M.p. 63-64°. Consequently, the isolated material was pure pyrocatechol diacetate.

Fraction II was redistilled to isolate the major fraction of the product with a b.p. of 126-128°/11 mm, n_D^{20} 1.5455, which was the above-described diacetyl derivative of phenylarsinous acid.

Saponification of $C_6H_5As(OCOCH_3)_2$. 3.2 g of the diacetyl derivative of phenylarsinous acid was mixed with 50 ml of water. The mixture was heated to boiling, and then remained for several days at room temperature. The white precipitate was filtered, washed with water, and dried to constant weight. M.p. 123-125°.

Found %: As 44.48, 44.58.

$C_6H_5AsO=O$. Calculated %: As 44.59.

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REACTION IN THE SYSTEMS CARBOXYLIC ACID-THIONYL CHLORIDE. A NEW TYPE OF CATIONIC CATALYSIS

M. Ya. Kraft and V. V. Katyshkina

(Presented by Academician A. N. Nesmeyanov, February 11, 1956)

In a preceding communication [1], we showed that the reaction of phenols with phosphoryl chloride, which leads to the formation of acyl chlorides of arylphosphoric acids, is considerably accelerated in the presence of neutral salts of the elements of Group I (NaCl, KCl). In addition, it was established that the activity of the catalyst, NaCl for example, depends to a great extent on the dissociation constant of the phenol - the higher the dissociation constant, the more effective is the addition of the neutral salt. Nitrophenols can react with POCl₃ only in this way, since they do not react with POCl₃ without the addition of the neutral salt. This observation permits formulation of a hypothesis on the reaction mechanism of this new type of cationic catalysis discovered by us, according to which the action of sodium chloride is explained by the distribution throughout the reaction medium of sodium ions with the formation of a certain, though of course a very insignificant, amount of phenolate (sodium picrate for example) which instantly reacts with the POCl₃ with the formation of the acyl chloride of the arylphosphoric acid. In addition, naturally, the NaCl is regenerated, and the reaction cycle continues until all of the phenol is reacted.

The expressed hypothesis on the mechanism of the action of neutral salts indicates that the new type of cationic catalysis can be extended to a series of other reactions. The conditions required for this must be: 1) the first component must possess a clearly expressed acid nature; 2) the second component must be a compound with a very mobile halogen atom and, moreover, must have a sufficiently high dielectric constant - it must be an ionizing solvent so that the above-mentioned distribution of cations can proceed.

From this point of view, the well-known reaction of carboxylic acids with thionyl chloride is of great interest, this reaction being the best known and a long known method for the preparation of acyl chlorides of carboxylic acids [2]. Indeed, the assumption has been repeatedly expressed [3] that this reaction proceeds with the intermediate formation of a mixed acyl chloride:



which is unstable and breaks down with the formation of the acyl chloride of the carboxylic acid and SO₂.

The first component - the carboxylic acid - completely satisfies the stated conditions; and thionyl chloride is a quite reactive substance, and, its dielectric constant being amply high (9.05), is an ionizing solvent [4].

Thus it was of considerable interest to determine whether the reaction of carboxylic acids with thionyl chloride is catalyzed by neutral salts. This reaction interested us because certain carboxylic acids, trichloroacetic acid for example, react very sluggishly with SOCl₂. Boeseken [5] prepared the acyl chloride of trichloroacetic acid in 30% yield by heating the acid with SOCl₂ for 8 hours. McMaster et al., [6] were not able to prepare this acyl chloride under approximately the same conditions. Gerrard and Thrush [3] indicated that, upon boiling trichloroacetic acid with SOCl₂ for 12 hours, a large part of the acid was unchanged. Since trichloroacetic acid is a very strong acid ($K = 2 \cdot 10^{-1}$), it is obvious that redistribution of sodium ions between NaCl and trichloroacetic acid must proceed readily and, as a result of the reaction cycle

1. $\text{RCOOH} + \text{NaCl} \rightleftharpoons \text{RCOONa} + \text{HCl}$
2. $\text{RCOONa} + \text{SOCl}_2 = \text{RCOOSOCl} + \text{NaCl}$
3. $\text{RCOOSOCl} = \text{RCOCl} + \text{SO}_2$

the desired acyl chloride must be readily obtained. The course of the first reaction is considerably facilitated by the very poor solubility of HCl in boiling SOCl_2 .

We verified the assumptions which have been expressed by a study of the kinetics of the reaction of SOCl_2 with trichloroacetic ($K = 2 \cdot 10^{-7}$), dichloroacetic ($K = 3.3 \cdot 10^{-5}$), and monochloroacetic ($K = 1.5 \cdot 10^{-5}$) acids. It is obvious that the degree of dissociation of these acids in SOCl_2 solution will differ from the cited values; nevertheless, the order of the series will not change.

The experimental method was the following. The reactions were carried out at 78° , which was achieved by the use of a special flask with a jacket. The jacket contained ethyl alcohol, which was heated to boiling while the reaction was carried out. In the flask was placed the acid being investigated (0.05 M) and a large excess of pure (7) SOCl_2 (0.25 M). The added salt (NaCl, KCl, RbCl) was finely ground, and, in order to guarantee rapid saturation of the reaction mixture, a rather large amount (1 g) of it was used; since the solubility of all of these salts in the system carboxylic acid - thionyl chloride is very low, apparently less than 0.1%, it is possible to use a considerably smaller amount in carrying out the reaction (see below). Reaction rates were judged by the amount of liberated SO_2 and HCl, which were absorbed in an excess of 1 N NaOH.

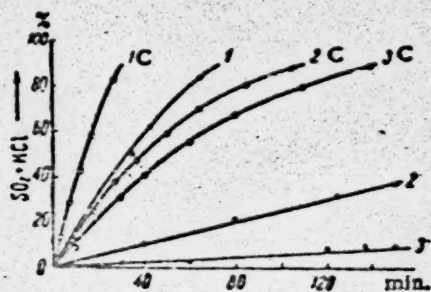


Fig. 1. Kinetics of the reaction of chloroacetic acids with SOCl_2 .

of the fact that the ratio of the reaction rates is inversely proportional to the times required for the reactions to proceed to equal per cents: $K_1/K_2 = t_2/t_1$.

Monochloroacetic acid is 50% reacted in 35 minutes, and, with the addition of KCl, in 15 minutes; hence, it follows that the reaction rate constant is increased 2.3 times by the addition of KCl. In the case of dichloroacetic acid, $t_1 = 175$ minutes and $t_2 = 40$ minutes; hence, we find that the rate constant is increased 4.4 times by the addition of KCl. In the case of trichloroacetic acid, we have $t_1 = 1700$ minutes and $t_2 = 55$ minutes; in this case, the rate constant is increased 30 times.

As may be seen, we have the greatest increase in reaction rate constant in the case of the strongest acid - trichloroacetic. This fact can be considered as confirmation of the above-assumed mechanism of the new type of cationic catalysis. On the other hand, the catalytic action of the neutral salts during the reaction of carboxylic acids with SOCl_2 can serve as indirect confirmation that the unstable mixed acyl chloride RCOOSOCl is an initial product of the reaction of carboxylic acids with SOCl_2 . The chlorides of different Group I elements have different catalytic activities, as may be seen from Figure 2, where are presented curves characterizing the reaction rates of trichloroacetic acid with SOCl_2 without a catalyst (Curve 1), with the addition of NaCl (2), with the addition of KCl (3), and with the addition of RbCl (4). The experiments were carried out exactly as the previous ones.

As can be seen, the most active catalyst was RbCl. Whether this depends on the different solubilities of the salts used in SOCl_2 or whether it indicates different activities of the cations is difficult to say at the present time; most probably, both factors have an effect. The effect of the amount of dissolved salt is clearly seen from those experiments in which we used organic cations. Salts of quaternary ammonium bases dissolve readily in the system carboxylic acid - SOCl_2 . We used trimethyl- β -bromoethylammonium bromide (bromocholine bromide). Upon the addition to the reaction mixture (0.05 M CCl_3COOH and 0.25 M SOCl_2) of 0.05 g of bromocholine bromide, the reaction proceeded to 56% of completion in 70 minutes; and with the addition of 1 g of this salt, the

corresponding time was 10 minutes. Naturally, in place of the quaternary ammonium salt, a tertiary amine can be added to the reaction mixture, since the formation of the salt in solution is guaranteed. For example, with the addition to the reaction mixture (of the same composition) of 0.05 g of pyridine, the reaction proceeded to 50% completion in 50 minutes, but with the addition of 1 g of pyridine, the reaction proceeded to 50% of completion in 7 minutes and was completed in 20 minutes. Attempts to use oxonium salts as catalysts (by the addition of ethyl ether to the reaction mixture) were unsuccessful; apparently, the basic properties of the cation were not sufficiently strong in this particular case. The catalytic phenomenon described in the present communication can be successfully used in all those cases where the reaction of the dicarboxylic acid with SOCl_2 proceeds sluggishly, and particularly in the case where the acid has a high dissociation constant. As an example, the acyl chloride of trichloroacetic acid was prepared by the described method.

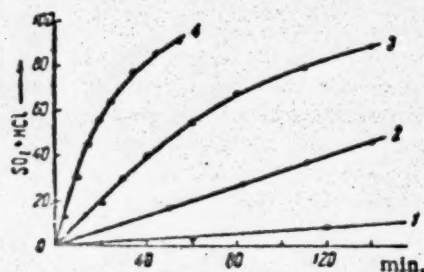


Fig. 2. Kinetics of the reaction of CCl_3COOH with SOCl_2 in the presence of NaCl , KCl , and RbCl .

A mixture of 98 g of trichloroacetic acid (0.6 M), 107 g SOCl_2 (0.9 M), and 2 g KCl was heated in a flask with a reflux condenser, (with a calcium chloride tube to prevent admission of moisture), bath at $80-85^\circ$. At first, vigorous evolution of a mixture of SO_2 and HCl was observed, which practically ceased after 7-8 hours. The cooled solution was filtered through a glass filter (No. 2) to remove calcium chloride, and was then distilled in a column. The yield of acyl chloride was 95 g, or 87% of theoretical. B.p. $114-115^\circ$ at 721 mm.

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HYDROGEN EXCHANGE REACTION OF CYCLOPENTADIENE

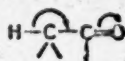
Associate Member of the Academy of Sciences USSR D. N. Kursanov and Z. N. Parnes

The chemical properties of cyclopentadiene (I) attest to the presence in the molecule of two hydrogen atoms which differ from the others, to wit, the hydrogen atoms of the methylene group. The special mobility of these hydrogen atoms is expressed in the ability of cyclopentadiene to yield metallic derivatives by reaction with certain alkali metals and also in its ability to form Grignard reagents [1]. Cyclopentadiene enters very readily into condensation reactions with ketones and aldehydes with the formation of fulvenes. It might be expected that the special nature of the two hydrogen atoms of the methylene group of cyclopentadiene would also find expression in hydrogen exchange reactions.

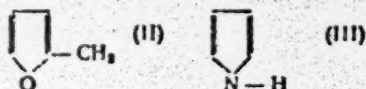
We decided to investigate the mobility of the hydrogen atoms in cyclopentadiene, using for this purpose the hydrogen exchange reaction with deuterium oxide in the presence of an alkaline catalyst: *N,N'*-dimethylpyridonimine.

It was shown that, not two, but all six hydrogen atoms of cyclopentadiene enter into the hydrogen exchange reaction with deuterium oxide in dioxane solution under extremely mild conditions.

This indicates that the special properties of the methylene-group hydrogens are not exhibited in the hydrogen exchange reaction. It should be noted that exchange equilibrium was attained after approximately 20 hours at 20°; i.e., under the same conditions under which even hydrogen atoms conjugated with a carbonyl group, in aldehydes and ketones for example, practically do not enter into hydrogen exchange reactions.



In order to investigate which grouping was responsible for the exchange of all six hydrogen atoms, we studied the hydrogen exchange of sylvan (II) and pyrrole (III).



This study showed that even under severe conditions (10 hours at 50° + 20 hours at 20°), sylvan exhibited practically no exchange and pyrrole exchanged only the one hydrogen joined to the nitrogen. Our data on the ability of pyrrole to undergo H-D exchange agree with the results of the work of Kolzumi and Titani [2]. However, we were not able to use their data directly, because the Japanese investigators conducted their experiments under conditions different from ours.

The inability of hydrogen atoms in the CH-groups of sylvan and pyrrole to exchange shows that in cyclopentadiene, which contains, just as do sylvan and pyrrole, the grouping $-\text{CH}=\text{CH}-\text{CH}=\text{C}<$, the group which is responsible for the mobility of the hydrogen atoms is the methylene group.

The increased mobility of the hydrogen atoms of the methylene group is usually explained by the conjugation of its C-H bonds with the two neighboring bonds of the cyclopentadiene ring. Although this consideration can explain the mobility of only two, but not of all six, hydrogen atoms, we investigated the hydrogen exchange reaction of cycloheptatriene, a molecule which also has a methylene group conjugated with two neighboring ethylenic bonds (IV).

It was shown, however, that, under the same conditions under which all six hydrogen atoms of cyclopentadiene exchange with deuterium oxide, cyclopentadiene did not enter into the hydrogen exchange reaction.

Consequently, it is necessary to search for another explanation of the ability of the hydrogen atoms of cyclopentadiene to exchange.

TABLE 1
Results of Experiments Carried Out at 20° for 22 Hours

Substance	Calculated for exchange of all H, γ/cc	Experimental, γ/cc	%
Cyclopentadiene	5190	4850	94
Cycloheptatriene	3140	25	1
Ferrocene	23580	325	1

TABLE 2
Results of Experiments Carried Out at 50° (10 hours) + 20° (20 hours)

Substance	Calculated γ/cc for exchange of		Experimental, γ/cc	%
	1 H	All H		
Pyrrrole	3325	5755	2895	87*
Sylvan	2035		65	3*
Ferrocene		9950	270	3
Cyclopentadiene		4440	4150	93

* % exchange from values calculated for one hydrogen atom.

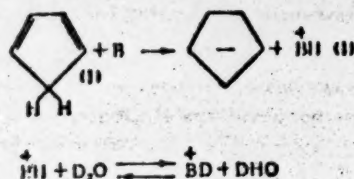
In 1931, Hückel [3], using the molecular orbital method, showed theoretically that the cyclic grouping of five CH-groups must have stability and aromaticity in the case of an anion (V). The cyclic grouping of seven CH-groups must have stability and aromaticity if it is a cation (VI).



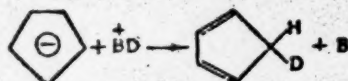
Further, these conclusions have received experimental confirmation, particularly in the work of Doering on the synthesis of tropylium salts [4], and also in investigations of ferrocene and its analogs [5-7], as a result of which the aromatic nature of these compounds was established.

Let us consider the hydrogen exchange reaction of cyclopentadiene from the point of view of these concepts.

The first step in the reaction is the splitting off of a proton from the methylene group by the action of a base (B), which, in our case, was N,N'-dimethylpyridonimine. This reaction is considerably facilitated by aromatic stabilization of the cyclopentadienyl anion which is formed.



The newly formed base – the cyclopentadienyl anion – reacts with BD^+ (or D_2^+) with the formation of deuterocyclopentadiene and the original base B (or OD^-).



Much repetition of the steps establishing acid-base equilibrium [Equations (1) and (2)] will lead to the exchange of all six hydrogen atoms of cyclopentadiene only under the indispensable condition that the negative charge of the cyclopentadienyl anion is not located at any one specific carbon atom.

If the base B is absent, the first step of Reaction (1) will not proceed, and, consequently, hydrogen exchange by cyclopentadiene does not proceed. Indeed, experiments showed that cyclopentadiene does not enter into hydrogen exchange reaction in either a weakly acid or a neutral medium (Table 3).

TABLE 3
Results of Experiments on Hydrogen Exchange by Cyclopentadiene in Neutral and Acid Medium (20°, 22 Hours)

Medium	Calculated γ/cc for exchange of		Experimental γ/cc
	2H	6H	
Neutral	3745	4880	85
19% H_2SO_4	5415		70
15% H_2SO_4	4415	5900	150

According to the calculations of Hückel [3], in the case of cycloheptatriene the formation of a cycloheptatrienyl anion must be considered highly improbable. As a consequence of this, the hydrogen exchange reaction does not proceed.

We do not see a possibility of interpreting our data otherwise than from the point of view of Hückel's concept, according to which the cyclopentadienyl anion has an aromatic nature and its negative charge is not localized at any one carbon.

In connection with the above, it seemed interesting to us to investigate also the ability of ferrocene (VID) to exchange. It was shown that ferrocene practically does not enter into a hydrogen exchange reaction. In this case, if the bond of the atom of iron with the cyclopentadiene residue were purely ionic, it would be expected that ferrocene would enter into a hydrogen

exchange reaction. The absence of exchange shows that this bond must be considered covalent.

EXPERIMENTAL

The analyses for deuterium content were carried out by R. G. Kononova.

The experiments were carried out using the materials in the following ratios: 0.1 mole of substance,

1 g of D_2O , and 0.1 g of dimethylpyridonimine. Purified dioxane was added to the mixture to a total volume of 50 mL. After the experiment, the investigated substance was separated, purified by distillation or crystallization, and burned. The excess density of the water of combustion, purified by the usual method, was then measured by the float method. The cyclopentadiene used in the experiments was prepared by depolymerization of the dimer and had a b.p. of 41-42°; n_D^{20} 1.4445.

At the conclusion of an experiment, the cyclopentadiene was distilled off under vacuum (80 mm) and collected in a trap cooled with liquid nitrogen. It was then dried over $CaCl_2$ and distilled at ordinary pressure, the fraction boiling at 41-43° being collected.

The cycloheptatriene was kindly presented to us by M. E. Volpin, to whom we express our appreciation. The cycloheptatriene used in the experiments contained 9% toluene. B. p. 113.1-113.3° (735 mm); n_D^{20} 1.5192. The absence of hydrogen exchange by the toluene was confirmed by a special experiment. At the conclusion of the experiment on hydrogen exchange by cycloheptatriene, pentane and cold water were added to the solution. The pentane layer was separated, dried, the pentane distilled off, and the cycloheptatriene distilled.

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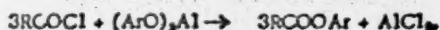
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PREPARATION OF ESTERS AND HYDROXYKETONES BY ACYLATION OF ALUMINUM PHENOLATES AND ARYL BORATES

V. K. Kuskov and L. P. Yuryeva

(Presented by Academician S. L. Volkovich, February 18, 1956)

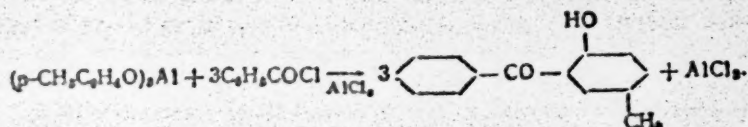
In the present work, we prepared aromatic esters of carboxylic acids by acylation of aluminum phenolates with equivalent amounts of acyl chloride:



Phenyl acetate, phenyl benzoate, and *p*-cresyl benzoate were prepared in yields close to theoretical.

The reaction proceeds at water-bath temperature. Heating to 160° leads to rearrangement of part of the ester into the hydroxyketone; evidently, due to aluminum chloride formed in the course of the reaction, the Fries reaction occurs [1]. The aluminum phenolates were prepared in quantitative yield by dissolving aluminum turnings in the appropriate phenol [2]. This means of preparing aromatic esters is satisfactory as a preparative method.

If a mixture of an aluminum phenolate and an acyl chloride is heated until solution takes place, then treated with aluminum chloride, and again heated, then instead of the ester, a hydroxyketone is obtained in good yield. For example, 2-hydroxy-5-methylbenzophenone is obtained in almost quantitative yield:



The course of the reaction differs from the Fries reaction. The total amount of aluminum chloride in our method of synthesis is 0.83-0.73, and even 0.5, mole per mole of acyl chloride (additionally, it is possible that 1/3 mole is formed in the reaction), which is less than in the Fries reaction, which requires 1.2-1.3, and sometimes up to 2, moles of aluminum chloride per mole of ester [3,4]. Further, when carrying out the Fries reaction with phenyl acetate in benzene, much acetophenone is obtained; i.e., the benzene acts as one of the reagents [5]. We found that acetylation of aluminum phenolate by acetyl chloride takes place successfully in benzene; *o*- and *p*-hydroxyacetophenone are obtained in good yield (85%), and there is absolutely no acetophenone formed; i.e., the benzene does not enter into the reaction. We also note that ratios of hydroxyketones obtained in our reaction frequently differ from the ratios obtained in Fries reactions.

It is noteworthy that sometimes the quantity of aluminum chloride is less than equimolar with respect to the acyl chloride (and to the hydroxyketone obtained), for example, in the preparation of hydroxybenzophenones. It is possible that direct acylation of the aluminum phenolate occurs. It is understood that the possibility is not excluded that the reaction partially proceeds through the ester stage.

Attempts to prepare hydroxyketones with smaller amounts of aluminum chloride did not yield positive results; a mixture of hydroxyketone and ester was obtained.

On acylation with benzoyl chloride of an analog of aluminum phenylate - triphenyl borate - phenyl benzoate was obtained in a yield of 75%. By acylation of tri-*p*-cresyl borate with benzoyl chloride in the presence of 1.33 moles of aluminum chloride (per mole of acyl chloride), the corresponding hydroxyketone, 2-hydroxy-5-methylbenzophenone, was obtained (80%).

EXPERIMENTAL

The experiments were carried out in a three-necked flask fitted with a stirrer, a reflux condenser, a dropping funnel, and a thermometer.

I. Preparation of Esters

Phenyl benzoate. To a suspension of 30.6 g (0.1 mole) of aluminum phenolate in 50 ml of benzene was added dropwise over a 30-minute period 42.2 g (0.3 mole) of benzoyl chloride. The flask was then heated for 30 minutes on a water bath, the phenolate going into solution. The mixture was allowed to stand for a day, after which, with water cooling, 200 ml of 8% hydrochloric acid, not above 30°, was added dropwise. It was then heated for 10 minutes on a water bath and cooled. That part of the phenyl benzoate which had precipitated was filtered, and the benzene layer was separated and the benzene distilled off; the residue was phenyl benzoate; the product was dried in air; the yield was 58 g (98% of theoretical); m.p. 69° (from alcohol).

***p*-Cresyl benzoate.** This ester was prepared similarly, but without a solvent, from 34.8 g (0.1 mole) of aluminum *p*-cresylate and 42.2 g (0.3 mole) of benzoyl chloride. The yield was quantitative; m.p. 71° (from alcohol).

Phenyl acetate. To 30.6 g (0.1 mole) of aluminum phenolate in 50 ml of dry benzene was added dropwise over a 1.5-hour period 23.6 g (0.3 mole) of acetyl chloride. Further treatment was the same as during the preparation of the phenyl benzoate; the product was purified by distillation. The yield was 34.3 g (84%); b.p. 195-197°; n_D^{20} 1.5093.

II. Preparation of Hydroxyketones

Hydroxybenzophenones. 30.6 g (0.1 mole) of aluminum phenolate and 42.2 g (0.3 mole) of benzoyl chloride were heated 30 minutes on a water bath. 33.4 g (0.25 mole) of freshly sublimed aluminum chloride was introduced into the flask, and the contents were heated for 30 minutes on a sand bath to 160-170°. 200 ml of 8% hydrochloric acid was added dropwise while cooling, and the mixture was then heated 10 minutes to boiling; the mixture was cooled, and the orange precipitate of a mixture of hydroxybenzophenones was filtered and dried in air; the weight was 59 g (quantitative yield), m.p. 110-112°. *o*-Hydroxybenzophenone was distilled from this mixture with superheated steam, extracted with ether, dried, and distilled. 13 g (22%) of *o*-hydroxybenzophenone was obtained; m.p. 35° (from alcohol); m.p. of the 2,4-dinitrophenylhydrazone, 249-249.5° [6]. After the steam distillation, 41.2 g (69.4%) of *p*-hydroxybenzophenone remained in the flask; m.p. 135° (from alcohol), which agrees with the literature data [7]. If the amount of aluminum chloride is reduced to 20 g (0.15 mole), 16.8 g (28.3%) of *o*- and 37 g (62.2%) of *p*-hydroxybenzophenone are obtained.

2-Hydroxy-5-methylbenzophenone. This compound was prepared from aluminum *p*-cresylate using a procedure completely analogous to that used for the preparation of hydroxybenzophenone. The yield was 61 g (96%); after distillation with superheated steam, the yield was 55.5 g (81.3%). M.p. 83-84° (from alcohol), which agrees with the literature data [1].

Hydroxyacetophenones. 33.4 g (0.25 mole) of aluminum chloride was introduced into a suspension of 30.6 g (0.1 mole) of aluminum phenolate in 35 ml of benzene, and 23.7 g (0.3 mole) of acetyl chloride was then added dropwise over a 6-hour period. The mixture stood for 15 hours and was then heated 2 hours on a water bath. On cooling to 20-30°, the mixture was hydrolyzed by adding dropwise 200 ml of 8% hydrochloric acid and then heating to boiling. On cooling, a benzene and a water layer separated, and the water layer was twice extracted with 15 ml of benzene. The combined benzene solutions were extracted with 15 times with 3% KOH. The alkaline extract was acidified with hydrochloric acid, and the *o*-hydroxyacetophenone was steam distilled. The distillate was extracted with ether, dried over $MgSO_4$, and distilled; the fraction boiling at 74-76°/2 mm was collected; 12 g (29.4% of theoretical) was obtained; n_D^{20} 1.5612; m.p. of the semicarbazone was 209°, which agrees with the literature data [8]. The hot solution remaining after the steam distillation was filtered and cooled; 20.8 g of *p*-hydroxyacetophenone crystallized. In addition, 3.1 g

was extracted with ether from the mother liquor for a total yield of 23.9 g (58.7%); m.p. 109°; m.p. of the semicarbazone 199°, which corresponds with the literature data [9]. The total yield of o- and p-hydroxyacetophenones was 88.1%.

2-Hydroxy-5-methylacetophenone. 23.6 g (0.3 mole) of acetyl chloride and 34.8 g (0.1 mole) of aluminum p-cresylate were heated for 30 minutes on a water bath. 33.4 g (0.25 mole) of aluminum chloride was introduced, and the mixture was heated 30 minutes at 160-170°, after which the usual separations were made. The yield was 40 g (88.9%); 35.8 g (79.6%) after steam distillation; m.p. 49° (from ligroin), which agrees with the literature data [8].

2-Hydroxy-5-methylpropiophenone. This compound was prepared from 34.8 g (0.1 mole) of aluminum p-cresylate, 27.9 g (0.3 mole) of propionyl chloride, and 20 g (0.15 mole) of aluminum chloride. The conditions were the same as in the preceding experiment. The yield was 40.4 g (82.1%); it boiled at 94-100°/2 mm, and at 115-117°/5 mm on redistillation; n_D^{20} 1.5480; m.p. of the semicarbazone 211°, which agrees with the literature data [8].

2-Hydroxy-5-methylbutyrophenone. This compound was prepared analogously to the preceding, using an equivalent amount (32 g) of butyryl chloride and 29.4 g (0.22 mole) of aluminum chloride. The yield was 45 g (84.3%); m.p. 33° (from methanol); semicarbazone m.p. 186°, which agrees with the literature data [10].

2-Hydroxy-5-methylbenzophenone from tri-p-cresyl borate. 33.2 g (0.1 mole) of tri-p-cresyl borate and 42.2 g (0.3 mole) of benzoyl chloride were heated 30 minutes on a water bath, cooled, 53.4 g (0.4 mole) of aluminum chloride was introduced, and the mixture maintained at 150-170° for 1.5 hours. Further treatment was as in the preparation from aluminum p-cresylate. The yield was 51 g (80%).

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EXHAUSTIVE CLEAVAGE OF THE HUMIC ACIDS OF PULVERULENT LIGNITE BY METALLIC SODIUM IN LIQUID AMMONIA

T. A. Kukharenko and T. E. Vvedenskaya

(Presented by Academician A. V. Topchiev, November 11, 1955)

It has previously been shown by us that the humic acids of solid fuels react with metallic sodium in liquid ammonia [1]. During this reaction, along with the solid residue which retains the properties of the humic acids, there are formed low molecular, ether-soluble products, and also water-soluble compounds, which are separable into fulvic acids and hydrocarbons. The mechanism of this reaction, by analogy with the reaction of lignin [2], is chiefly a splitting of the ether bonds between the basic structural links in the molecules of the humic acids. By single cleavage of different humic acids it was found that the number of ether bonds in the molecules of the humic acids of the coal decreased on passage from samples of lower stages of carbon formation to samples of higher stages.

TABLE 1

The Course of Successive Cleavage of Humic Acids by Metallic Sodium in Liquid Ammonia

Cleavage No.	No. of experiment	Humic acids (org. sub.) g	Yield of solid residue		% cleavage and loss	Cleavage no.	No. of experiments	Amount of humic acids (org. sub.) g	Yield of solid residue		% cleavage and loss
			g	%					g	%	
1	10	153.13	122.85	80.40	19.60	8	2	23.63	20.56	87.00	13.00
2	9	115.18	92.0	79.8	20.12	9	1	16.33	14.49	88.73	11.27
3	7	86.12	73.29	85.10	14.00	10	1	11.73	10.25	87.38	12.62
4	5	70.50	59.98	85.07	14.83	11	1	8.57	7.19	83.89	16.11
5	4	55.75	46.16	82.79	17.21	12	1	4.83	3.96	81.99	18.01
6	3	42.14	35.33	83.83	16.17	13	1	2.89	2.18	75.44	24.56
7	2	30.18	26.57	88.03	11.97	14	1	1.22	0.82	—	—

That ether bonds are chiefly basic bonds in the molecules of humic acids and are not found in the peripheral part is substantiated by observation of the course of successive cleavage of the same sample of humic acids. In the present work, repeated cleavage of the humic acids* of pulverulent lignite of the Babaevq formation was carried out with metallic sodium under the indicated conditions. In Table 1 are presented the data on the yield of solid residues from 14 successive cleavages. From these data it follows that the solid residue not entering into the preceding reaction with sodium reacts during succeeding treatments down to complete cleavage. The per cent cleavage exhibits a certain variation, but a tendency toward decrease is not observed. The products formed during successive treatments have similar properties.

The solid residues obtained during successive cleavage were investigated. In Table 2 are presented the

* The sample was the water- and ether-insoluble part of the humic acids, which is relatable, according to the Oden classification, to humic acid.

elemental compositions of the solid residues and the content of active acid groups. The data of this table show that the solid residues of the successive cleavage of humic acids by metallic sodium have compositions approximating that of the original humic acids. At the same time, no specific regularity was noted in the variations in elemental composition. The content in the residues of phenolic hydroxyls was somewhat lower and that of carboxyl groups was higher than in the original acids.

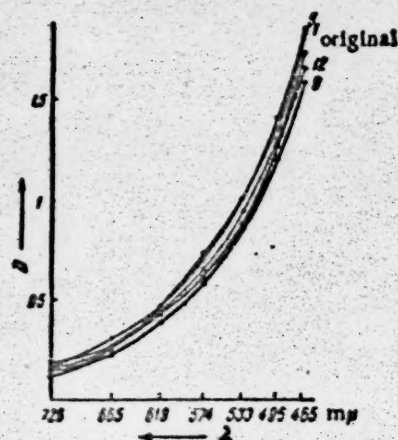


Fig. 1. Optical density of alkaline solutions of the solid residues of the successive cleavage of humic acids by metallic sodium.

The similarity in composition of the original humic acids and the solid residues from cleavage is also confirmed by optical density values of 0.02% alkaline solutions of each. As seen from Figure 1, the optical density, for light of various wave lengths, of the original humic acids and those of the solid residues from successive cleavages practically lie on one curve.

The same thing follows from Figure 2, where are presented the viscosities at a temperature of 20° of different concentrations of solid residues from the cleavage of humic acids. The viscosity is the same for all preparations at the lower concentrations and decreases somewhat with increasing concentration of residues from cleavages succeeding the first.

The stability toward the coagulating action of barium chloride, which characterizes the degree of dispersion of the humic acids, is also practically the same. This can be seen from the data of Table 2, where are presented the coagulation thresholds with respect to barium chloride of the original humic acids and of the solid residues from the cleavages.

X-ray analysis also indicated the similarity of the original humic acids and the solid cleavage residues; the Debye radiograms of both were similar (L. L. Razumova).

TABLE 2

Compositions of Solid Residues from Successive Cleavage of Humic Acids by Metallic Sodium

Sample (Cleavage No.)	Elemental composition, %		Content of active acid groups, mg. eqv./g			Properties of 0.02% alkaline solution	
	C	H	Total	Carboxyl	phenyl hydroxyl (by dif- ference)	optical density, violet region	coagula- tion thresh- old, mg. eqv. BaCl ₂ / liter
Original humic acids	63.97	4.56	6.98	1.81	5.17	1.75	20
1	62.82	4.71	7.25	2.59	4.66	1.85	20
2	61.71	5.26	7.46	3.13	4.33	1.82	20
3	59.94	4.88	7.78	3.82	3.96	2.00	20
4	59.72	5.35	7.36	2.95	4.41	1.67	18
5	59.65	5.45	7.12	2.84	4.28	1.88	—
6	61.53	5.03	6.78	2.52	4.24	1.77	20
7	61.22	5.06	5.43	2.54	2.89	1.67	17
8	63.57	5.08	5.76	2.80	2.96	1.75	20
9	64.58	5.09	5.34	3.18	2.16	1.69	18
10	65.50	5.12	5.44	2.38	3.06	1.82	20
11	64.95	5.58	5.27	2.57	2.70	1.47	—
12	63.91	4.91	5.55	3.27	2.28	1.67	—
13	63.70	4.92	6.78	2.87	3.61	—	—
14	62.40	5.06	6.24	2.90	3.34	—	—

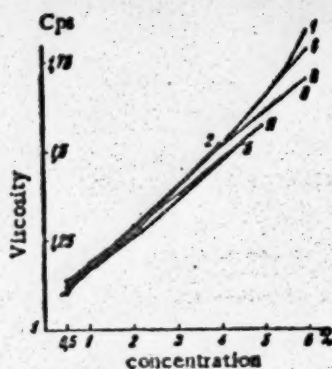


Fig. 2. Variation with concentration of the viscosity of alkaline solutions of the solid residues from successive cleavages of humic acids.

Thus, all of the data presented indicate the similarity in composition and properties of the initial humic acids and the residues from successive cleavage by metallic sodium in liquid ammonia down to complete decomposition, and the data also indicate the constancy of the percentage of cleavage. The data presented confirm the previously made assumption concerning the mechanism of this process as a reaction proceeding mainly by cleavage of ether bonds, which are the basic type of structural links in the molecule. The reaction proceeds like a typical heterogeneous reaction characteristic of high molecular organic compounds with unequal participation of the individual molecules.

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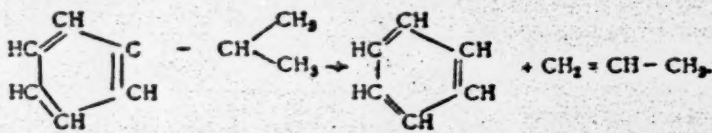
A STUDY OF CUMENE CRACKING OVER DEUTERATED SILICA-ALUMINA CATALYST

G. M. Panchenkov, Z. V. Gryaznova and V. M. Emelyanova

(Presented by Academician B. A. Kazansky, January 3, 1956)

The majority of investigators working on the study of silica-alumina catalysts connect the activity of these catalysts with the presence of hydrogen ions in them. Therefore, it seemed expedient to substitute deuterium ions for the hydrogen ions of the catalyst and to study its behavior in the reaction. It was necessary to use a well-studied reaction for this purpose. The reaction selected was that of cumene cracking [1-4].

The basic cracking reaction can be represented thus:



The kinetics of this reaction, as has been shown in [1, 2, 5-7], are described by the equation:

$$k = n_0 \frac{R}{bI} \{-\ln(1-x) - x\};$$

where $k = k^*S_0$, k^* being the true reaction rate constant; S_0 is the surface of the catalyst per unit of bed depth; n_0 is the number of moles of the original material [feed] entering the reaction zone per unit time; b is the adsorption coefficient of the feed material; $I = \sum(\nu_i b_i)$, the sum of the products of the adsorption coefficients and the stoichiometric coefficients for the cracked products which inhibit the process; I is the catalyst bed depth; x is the quantity of reacted material in relative units.

The exchange of hydrogen by cumene and its cracking products, benzene and propylene, both separately and in equimolar mixtures of benzene and propylene, was studied by us with respect to its dependence on feed rate and reaction temperature.

Three catalysts were used in the work: pure aluminum oxide, silica gel, and a silica-alumina catalyst having the composition 32.75% Al_2O_3 and 67.25% SiO_2 , which was prepared from the same gels from which the Al_2O_3 and the silica gel were prepared. The silica-alumina catalyst was prepared by mixing silicic acid and aluminum hydroxide hydrogels, using the method developed by G. M. Panchenkov and K. V. Topchieva [8]. The catalyst contained 190 m-equiv. D per 100 g of catalyst, which was close to the maximum deuterium content obtainable by exchange of hydrogens of the catalyst for the deuterium of heavy water under the conditions of our experiments. The cumene was prepared from technical cumene which was purified by boiling for three hours over metallic sodium and then distilling from a Favorsky flask. The fraction collected boiled in the range 149.5-150.5° and had an index of refraction of n_D^{20} 1.4919 (according to the literature data, n_D^{20} 1.4920 [9]). For further purification, the cumene was distilled in a column of 33 theoretical plates; however, this did not change the refractive index.

The catalytic cracking of the cumene was carried out by the flow method in a quartz apparatus. The apparatus consisted of a catalyst tube with nichrome-wire winding, this tube being located in a quartz tube of greater diameter in order to reduce heat losses. The reactor temperature was measured by means of a chromel-alumel thermocouple inserted in a thermowell which was disposed along the axis of the reactor. The temperature of the

furnace was regulated by an autotransformer. Variations in furnace temperature along the length of the catalyst did not exceed 1°. The cumene was automatically fed to the catalyst tube by means of a synchronous motor and a medical syringe.

Silica-alumina catalyst in an amount of 11 g (25 ml) was mixed with quartz packing to reduce the resistance of the catalyst bed and charged into the reaction. After a run, the catalyst was regenerated by passing dry air through it at a temperature of 500-550°. The reaction products were condensed in a condenser and collected in a Favorsky flask connected to the reactor by means of ground joints. Gaseous reaction products from the Favorsky flask passed into another condenser and were collected in a eudiometer. At the end of a run, the Favorsky flask, together with the second condenser, was disconnected from the apparatus. The flask was covered with a ground cover having a hook for suspension of a thermometer, and the liquid fraction was distilled, fractions boiling in the ranges 75-85° and 148-152° being collected. All parts of the apparatus were connected with each other by means of ground joints.

TABLE 1
Cumene Cracking and Exchange by Cumene and Its Cracking Products in This Process at 450°

Space rate*	Conversion of cumene by cracking, %	Excess density of combustion water, γ		
		unreacted cumene	propylene	benzene
0.132	62	1779	1254	1378
0.192	63	638	855	917
0.216	65	584	671	824
0.264	65	5	10	33

* In all tables, space rate = $\frac{\text{volume of material}}{\text{volume of catalyst} \cdot \text{hour}}$

Analysis of the gases formed in the reaction was carried out in a VTI apparatus. Combustion of the reaction products (benzene, cumene, and propylene) was carried out over copper oxide in a quartz apparatus. Water for analysis was purified by passage over copper oxide at a temperature of 700°, and then in quartz apparatus for the purification of small amounts of water [10]. Analysis of the water for excess density was carried out by the densimetric method [11]. The excess density of the water was calculated from the formula $\Delta d = \alpha \Delta t$ in units of γ , where Δt is the difference in temperature of flotation equilibrium in excess-density water and in standard water. α is the change in the density of water per degree. Between 20 and 30°, $\alpha = 257 + 9.6(t - 25)$. The standard water was prepared by the usual method. Every dish used in the work was made of quartz.

Owing to the small amount of water analyzed, the latter had to be diluted. Since the weighings were carried out on analytical scales having an accuracy of ± 0.0001 g, the accuracy of the analyses was within 1 to 5%. The experimental results are presented in Tables 1, 2, and 3.

That the per cent cumene conversion in the reaction did not depend on space rate (Table 1) indicates that a state of chemical equilibrium was attained in all cases. Thermodynamic calculations completely confirm this. Indeed, the per cent cumene conversion at equilibrium is very close to the results obtained by us. The small variations in per cent cumene conversion at the different rates are explained by experimental error and the ability of the catalyst to "develop" in the course of the work. In order to get out of the equilibrium region, it was necessary to increase the cumene feed rate. However, as seen from Table 1, this cannot be done, since the hydrogen exchange reaction completely ceases with an increase in rate above 0.264.

It follows from Table 2 that the reaction rate for hydrogen exchange between catalyst and hydrocarbons in the cracking process in the range 500 to 350° depends very little on temperature.

The results obtained during the investigation of the exchange of hydrogen of benzene, propylene, and their equimolar mixtures for the deuterium of the catalyst are presented in Table 3. The benzene and propylene were fed to the catalyst at rates close to those at which they passed through the catalyst in the cumene cracking process.

From Table 3 it is apparent that the amount of hydrogen exchanged by the reaction products from cumene cracking over deuterated catalyst was close to the amount exchanged during passage of pure benzene and propylene over deuterated catalyst.

* VTI = All-Union Heat Engineering Institute - Publisher.

TABLE 2

Cumene Cracking and Exchange of Hydrogens Between the Substances and Catalyst in This Process at Various Temperatures

Temperature, °C	Space rate	% cumene conversion from cracking	Excess density of combustion water, γ		
			cumene	propylene	benzene
500	0.264	68	—	740	667
500	0.192	70	—	1026	1050
450	0.192	63	638	855	917
400	0.192	30	720	1030	915
350	0.192	24	775	977	900

TABLE 3

Exchange of Hydrogens of the Products of Cumene Cracking for Deuterium of the Catalyst at 450°

Substance	Space rate	ml/hour	Excess density of the combustion water, γ	
			passed over deuterated catalyst	Obtained from cracking cumene over deuterated catalyst
Benzene	0.132	—	1355	1343
Propylene	—	600	2183	1780
Equimolar mixture of benzene and propylene	0.132	—	11	33
—	—	780	13	10
Equimolar mixture of benzene and propylene	0.086	—	580	917
—	—	480	620	855

Considering the results obtained during the study of cumene cracking over deuterated catalyst, it is possible to come to the conclusion that hydrogen exchange for deuterium by cumene and its cracking products is an independent reaction proceeding independently from the cumene cracking reaction. That with an approximately two-fold change in the cumene feed rate (from 0.130 to 0.264 volumes of material volume of catalyst/hour) the exchange reaction practically dies out while the per cent cumene conversion resulting from the cracking of cumene remains constant, as seen from Table 1, confirms the independence of the hydrogen exchange reaction.

Cracking does not occur over deuterated aluminum oxide with a content of $145 \frac{\text{m-equiv. D}}{100 \text{ g Al}_2\text{O}_3}$ when feeding cumene at a space rate of 0.13 and at a temperature of 450°, but exchange does take place. The excess density of the water obtained after combustion of cumene passed over deuterated aluminum oxide catalyst at the indicated conditions was 500 γ . After passing cumene over the catalyst, the activity of the aluminum oxide was verified by dehydration of ethyl alcohol, which indicated a high activity for the aluminum oxide.

Over deuterated silica gel at a temperature of 450° and at a space rate of 0.13, neither cumene cracking nor exchange of the hydrogen of cumene for deuterium of the catalyst was observed.

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INTERCONVERSIONS OF DIPEPTIDES AND THEIR ANHYDRIDES

K. T. Poroshin, T. D. Kozarenko and Yu. I. Khurgin

(Presented by Academician V. A. Kargin, December 28, 1955)

The presence of cyclic structures both in the products of albumin hydrolysis and in the products of the polycondensation of esters of α -amino acids, and sometimes also formed in the polymerization of anhydrides of N-carboxy- α -amino acids, lends considerable significance to the study of the interconversions of peptides, particularly dipeptides, and diketopiperazines. There are indications in the literature as to the relative ease of hydrolysis of diketopiperazines [1]. Fischer showed that hydrolysis of one of the peptide bonds of diketopiperazines proceeds readily in a strongly alkaline medium with the formation, after the addition of water, of the corresponding dipeptides. On the other hand, N. D. Zelinsky and N. L. Gavrilov [2], during an investigation of the composition of the products of autoclave hydrolysis of albumins by various acids, discovered that it is possible for anhydride formation to occur in a number of dipeptides. Brigl, Abderhalden and Komm, and Ludke [3] also found diketopiperazines after heating glycylglycine, dl-leucylglycine, and other dipeptides in an acid medium. Certain dipeptide derivatives undergo analogous transformations under milder conditions. Esters of dipeptides are comparatively readily converted into diketopiperazines [4]. This reaction is also observed in the course of the polycondensation of esters of α -amino acids, which imparts to it special significance. Huang and Nieman [5] also observed the formation of diketopiperazines upon warming primary amides of certain dipeptides in aqueous or methanol media.

Up to the present, no attention has been given to the possibility of the interconversion of dipeptides and their anhydrides in alkaline and neutral media. In studying polycondensation reactions of esters of α -amino acids, we also observed the absence of quantitative data on the behavior of dipeptides and diketopiperazines in an alkaline medium. Furthermore, this transformation is of special interest, since esters of α -amino acids are materials having a basic nature. It should also be kept in mind that interconversion reactions occur cleanly in an alkaline medium, since these reactions are not accompanied by hydrolysis of the dipeptides to amino acids, a reaction which is observed in an acid medium.

In connection with this, first of all we studied the stability of diketopiperazines in alkaline medium as a function of the hydrogen ion concentration. In addition to this, the kinetics of the alkaline hydrolysis of diketopiperazines and the behavior of dipeptides in alkaline and neutral media were studied. All experiments were carried out at a temperature of 40°, that is, under those conditions under which we had carried out polycondensation reactions [6].

The determination of the amount of linear and of cyclic structures was carried out, as before [7], by means of the content of amine nitrogen and also by the so-called "copper" method, that is, by the determination of the amount of copper bound by dipeptides in the form of a biuret complex. In those cases where the solutions investigated had an insufficient concentration of alkali for the complete formation of the complex [8], the required amount of a concentrated solution of alkali was added, and titration was carried out at a reduced temperature. Hydrolysis of the diketopiperazines was not noted during the time required for the titration (about 1 minute).

dl-Alanylalanine anhydride. The products of the polycondensation of the ethyl ester of dl-alanine were used for the preparation of alanylalanine anhydride, since, as is well known, these products contain considerable amounts of the diketopiperazine [6,7]. The anhydride was obtained according to Frankel and Katchalsky [9] by volatilization (140°/10⁻³ mm).

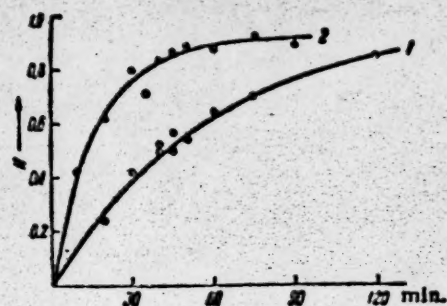


Fig. 1. Course of the hydrolysis of anhydrides. 1) dl-Alanine, 2) glycine. N) extent of hydrolysis in 0.1 N NaOH at 40°. A) Min.

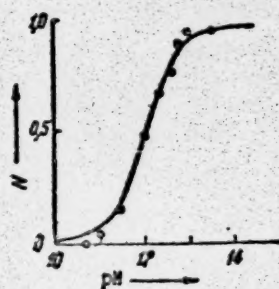
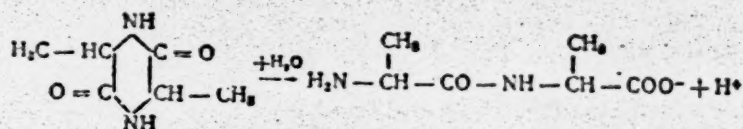


Fig. 2. Variation in the extent of the hydrolysis of alanylalanine anhydride with pH. N) extent of hydrolysis.



with a hydrolysis constant $K_h = \frac{[\text{H}^+][\text{dipeptide}]}{[\text{diketopiperazine}]}$, which, for the alanine anhydride, was equal to a pK_h of 12.0.

Glycylglycine anhydride. The glycylglycine anhydride was prepared according to Fischer [10]. Hydrolysis of the glycine diketopiperazine in alkaline medium at a temperature of 40° was concluded in the first hour of the reaction (Figure 1, 2). As in the case of the alanine anhydride, hydrolysis of the diketopiperazine is a first order reaction. The rate constant for this reaction was $9.63 \cdot 10^{-4} \text{ sec}^{-1}$. In Figure 3, 1, are presented the results of experiments studying the variation in the extent of hydrolysis of diketopiperazine with pH (at 40°). The experimentally obtained values of the extent of hydrolysis lie close to the theoretical curve calculated on the basis of the law of mass action using 10.8 for the hydrolysis constant, pK_h .

Further, the possibility of the reverse formation of diketopiperazines in a solution of glycylglycine at various pH values was investigated. The first experiments showed that, even in alkaline solution, bonding of the amine nitrogen and a decrease in the amount of bound copper according to the "copper" method takes place in a solution of glycylglycine. The experiments were carried out at 40° in solutions of NaOH and in borate and phosphate buffer solutions within the pH limits of 7.0 to 13.0. Bonding of the amine nitrogen was dependent on the formation of diketopiperazines, and not on the emergence of longer peptides, as was established by the differential spectrophotometric method [8]. Additional proof of the formation of anhydrides was obtained by identification of the reaction products by paper electrophoresis.

In 0.1 N NaOH at a temperature of 45°, hydrolysis of the diketopiperazine is practically complete in approximately 1.5 hours. The course of the hydrolysis of the diketopiperazine is shown in Figure 1, 3. The points on the graph represent the results of some measurements, by the "copper" method, of the amounts of dipeptides formed during the course of the alkaline hydrolysis of the diketopiperazine. The course of the hydrolysis of diketopiperazine with time shows that this reaction is first order. The reaction rate constant for the hydrolysis of the alanine diketopiperazine in alkaline medium is $K = 2.56 \cdot 10^{-4}$, on the basis of which was calculated the theoretical curve 1 in Figure 1. The reaction rate did not change with a decrease in pH, although complete hydrolysis of the diketopiperazine was not observed. In connection with this, the dependence of the extent of the hydrolysis of the diketopiperazine on pH was measured.

In Figure 2 are plotted the experimentally obtained values of the extent of hydrolysis at various values of pH. These results correspond to the amount of diketopiperazines, measured by the "copper" method and also by the increase in amine nitrogen, through a 2-hour period after initiation of the reaction, that is, up to a time at which it was practically complete. Accurately titrated solutions of NaOH and borate buffer solutions were used for the measurements. The variation in the extent of hydrolysis with pH followed rather accurately the law of mass action for the reaction.

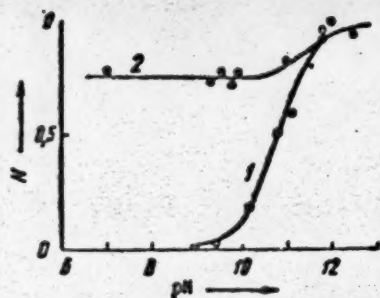


Fig. 3. Variation, with pH, of the extent of hydrolysis of glycylglycine anhydride (1) and of the decrease in the amount of glycylglycine (2).

conversion of dipeptide and diketopiperazine was observed, although it is only partially reversible.

An investigation of the kinetics of the formation of glycylglycine anhydride showed that this reaction is of not less than second order. However, in addition to this, the course of the reaction is somewhat unusual, since there is an induction period of the order of 30 minutes. The amount of anhydrides obtained is significantly less than the amount of unhydrolyzed diketopiperazines at the same pH values. At a pH of less than 10 (where the diketopiperazine is not hydrolyzed), the glycylglycine in the solution after standing for more than 1.5 hours (conclusion of the reaction) at 40° has formed anhydride only to the extent of ~25%. A similar extent of anhydride formation is observed even in water and in buffered solutions having a pH of 7. The dependence of the extent of anhydride formation on pH (Figure 3, 2) conforms to the law of mass action. Thus, inter-

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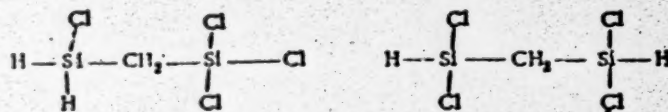
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SYNTHESIS OF ORGANOSILICON COMPOUNDS OF THE TYPE OF BIS(TETRAALKYLDISILANEMETHANE)CYCLODIOXIDE

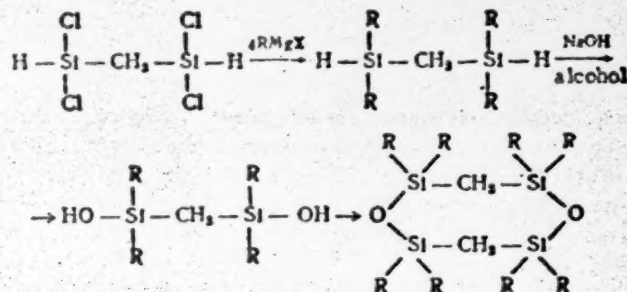
Academician A. V. Topchlev, N. S. Nametkin and L. S. Povarov

In previous communications [1-3] we described the synthesis of linear compounds with siloxane-carbon links on the basis of one of the products of the reaction of methylene chloride with silicon-pentachlorodisilanemethane.

N. S. Nametkin, A. V. Topchlev and O. P. Solovova [4] showed that the reaction of methylene chloride with silicon also results in the formation of tetrachlorodisilanemethane, for which two isomeric formulas can be assumed:



In the present work, the symmetrical structure of tetrachlorodisilanemethane was demonstrated by the preparation from it of tetramethyldihydroxydisilanemethane and bis(tetramethyldisilanemethane)cyclodioxide, both of which are described in the literature [5,6], and there was also shown the possibility of preparing from it cyclic compounds with siloxane-carbon links according to the following scheme:



EXPERIMENTAL

Preparation of tetramethyldisilanemethane. To methylmagnesium iodide, prepared from 400 g (2.8 moles) of methyl iodide and 68 g (2.8 moles) of magnesium in 500 ml of ether, was added, with stirring, 70 g (0.33 mole) of tetrachlorodisilanemethane dissolved in 150 ml of ether. At the conclusion of the addition, the reaction mixture was heated to boiling for 4 hours; it was then cooled to room temperature and decomposed with 10% hydrochloric acid. The ether was washed, dried, and distilled in a column. There was obtained 36 g (82.5% yield) of a material with a boiling point of 103° at 752 mm, which is characteristic of tetramethyldisilanemethane.

Found %: C 45.46, 45.38; H 12.18, 12.21.
 $C_6H_{12}Si_2$ Calculated %: C 45.39; H 12.19.

Preparation of tetramethyldiethoxydisilanemethane. To a solution of sodium alcoholate, previously prepared from 2.3 g of sodium and 50 ml of absolute ethyl alcohol, was added 10 g of tetramethyldisilanemethane. A reaction yielding tetramethyldiethoxydisilanemethane began immediately and was accompanied by the liberation of hydrogen. After the liberation of hydrogen had ceased, the mixture was heated to boiling for 15 minutes, then cooled to room temperature, and dry carbon dioxide was passed through the reaction mixture until the formation of the precipitate had ceased. The precipitate of sodium ethyl carbonate was separated in a centrifuge, and the alcoholic solution was distilled. There was obtained 8.5 g (51.2% yield) of a material boiling at 82-83° at 21 mm, which is characteristic of tetramethyldiethoxydisilanemethane.

Found %: C 49.34, 49.30; H 10.99, 10.89.
 $C_8H_{20}O_2Si_2$ Calculated %: C 49.04; H 10.98.

Preparation of bis(tetramethyldisilanemethane)cyclodioxide. To 100 ml of a 5% solution of sodium hydroxide in methyl alcohol was added 16 g of tetramethyldisilanemethane. Vigorous evolution of hydrogen occurred immediately. After hydrogen evolution ceased, the mixture was heated to boiling for 15 minutes, then cooled to 0°, and diluted with 150 ml of water. The precipitated crystals were suction filtered in a funnel and washed with water. After drying, there was obtained 12.5 g of a material which, after recrystallization from petroleum ether, melted at 30°, b.p. 208-209° at 760 mm, which properties are characteristic of bis(tetramethyldisilanemethane)cyclodioxide.

Found %: C 41.66, 41.08; H 9.70, 9.60.
 $C_{12}H_{24}O_2Si_4$ Calculated %: C 41.05; H 9.65.

Molecular weight: found, 296 and 288; calculated for $C_{12}H_{24}O_2Si_4$, 292.

Preparation of tetramethyldihydroxydisilanemethane. 8.5 g of tetramethyldiethoxydisilanemethane was added to 40 ml of distilled water in a quartz flask carefully washed from traces of acid and alkali. Upon standing for 5 days, the formation of crystals occurred. In the mixture. After this, the organosilicon products were extracted by heating with 100 ml of petroleum ether. The ether layer was quickly separated and cooled with crushed ice. The precipitated crystals were filtered, washed with cold petroleum ether, and dried in a vacuum desiccator. There was obtained 4.5 g of a crystalline material with a melting point of 86-87°, which is characteristic of tetramethyldihydroxydisilanemethane.

Found %: C 36.39, 36.50; H 9.94, 9.93.
 $C_6H_{14}O_2Si_2$ Calculated %: C 36.55; H 9.82.

Preparation of tetraethyldisilanemethane. To ethylmagnesium bromide, prepared from 174.4 g (1.6 moles) of ethyl bromide and 39 g (1.6 mole) of magnesium in 400 ml of ether, was added 40 g (0.18 mole) of tetraethyldisilanemethane dissolved in 100 ml of ether. The reaction mixture was heated to boiling for 6 hours, and decomposed with 10% hydrochloric acid. The ether layer was washed, dried, and distilled in a column. There was obtained 26 g (75.6% yield) of a material with a boiling point of 55° at 3 mm, which is characteristic of tetraethyldisilanemethane.

Found %: C 57.55, 57.40; H 12.84, 12.71.
 $C_8H_{24}Si_2$ Calculated %: C 57.37; H 12.94.

Preparation of tetraethyldihydroxydisilanemethane. To 120 ml of a 10% alcoholic solution of NaOH was added 26.5 g of tetraethyldisilanemethane. The mixture was heated to boiling for 4 hours. After the liberation of hydrogen had ceased, the reaction mixture was cooled to room temperature, diluted with 100 ml of petroleum ether, and then with 200 ml of water. The ether layer was separated, washed free of alcohol, filtered, and distilled. There was obtained 26 g (84% yield) of a material with a boiling point of 126-128° at 5 mm and a melting point of 17-18°, which values are characteristic of tetraethyldihydroxydisilanemethane.

Found %: C 49.16, 49.28; H 10.97, 10.89.
 $C_8H_{24}O_2Si_2$ Calculated %: C 49.04; H 10.98.

TABLE I

Formula	b.p., °C	Pressure, mm Hg	M.p., °C	d_4^{20}	n_D^{20}	MR _D	
						found	calculated
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{H}-\text{Si}-\text{CH}_2-\text{Si}-\text{H} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	103	752	—	0.7373	1.4140	44.80	45.08
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{H}-\text{Si}-\text{CH}_2-\text{Si}-\text{H} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	55–56	3	—	0.7974	1.4473	63.13	63.10
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{C}_2\text{H}_5\text{O}-\text{Si}-\text{CH}_2-\text{Si}-\text{OC}_2\text{H}_5 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	83–83	21	—	0.8603	0.4102	64.32	64.58
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{HO}-\text{Si}-\text{CH}_2-\text{Si}-\text{OH} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	—	—	86–87	—	—	—	—
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{HO}-\text{Si}-\text{CH}_2-\text{Si}-\text{OH} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	126–128	5	17–18	0.9536	1.4639	63.76	63.68
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{H}-\text{Si}-\text{CH}_2-\text{Si}-\text{OH} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	158–159	4	—	0.8635	1.4623	100.85	100.80
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{HO}-\text{Si}-\text{CH}_2-\text{Si}-\text{OH} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	185–187	5	—	0.9023	1.4624	101.41	101.18
$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \quad \\ \text{Si}-\text{CH}_2-\text{Si} \\ / \quad \backslash \quad / \quad \backslash \\ \text{O} \quad \text{Si}-\text{CH}_2-\text{Si} \quad \text{O} \\ / \quad \backslash \quad / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	208–209	760	30	0.9048	1.4345	84.30	84.32
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{Si}-\text{CH}_2-\text{Si} \\ / \quad \backslash \quad / \quad \backslash \\ \text{O} \quad \text{Si}-\text{CH}_2-\text{Si} \quad \text{O} \\ / \quad \backslash \quad / \quad \backslash \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	154–155	3	—	0.9361	1.4683	120.23	120.40
$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \quad \quad \\ \text{Si}-\text{CH}_2-\text{Si} \\ / \quad \backslash \quad / \quad \backslash \\ \text{O} \quad \text{Si}-\text{CH}_2-\text{Si} \quad \text{O} \\ / \quad \backslash \quad / \quad \backslash \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	214–216	1	—	0.8907	1.4649	195.24	195.44

• Literature data: m.p. 84–86° [5].

•• Literature data: b.p. 213–215°, m.p. 30°; d_4^{20} 0.9039; n_D^{20} 1.4341.

Preparation of bis(tetraethylidisilanemethane)cyclodioxide. 22 g of tetraethylidihydroxydisilanemethane was boiled with 50 ml of 40% hydrobromic acid for 6 hours, after which the mixture was cooled to room temperature, and the organosilicon products were extracted with ether. The ether extract was neutralized, washed with water, dried, and distilled. A fraction boiling at 162-164° at 4 mm was obtained, from which, by a second distillation over metallic sodium, there was obtained 15 g (74% yield) of a material with a boiling point of 154-155° at 3 mm, which is characteristic of bis(tetraethylidisilanemethane)cyclodioxide.

Found %: C 53.55, 53.44; H 10.94, 10.81.
 $C_{18}H_{44}O_2Si_4$ Calculated %: C 53.42; H 10.96.

Molecular weight: found, 402 and 398; calculated for $C_{18}H_{44}O_2Si_4$, 404.8.

Preparation of tetrabutoxydisilanemethane. A mixture of 274 g (2 moles) of butyl bromide, 75 g (0.3 mole) of pentachlorodisilanemethane and 300 ml of ether was added, with stirring, to 48.6 g of magnesium in 400 ml of ether. The reaction mixture was heated to boiling, with stirring, for 16 hours, and then decomposed with 10% hydrochloric acid. The ether layer was treated with a 10% solution of sodium carbonate, washed, dried, and distilled. The fraction boiling up to 190° at 8 mm was collected and afterwards distilled in a column. There was obtained 34 g (35.8% yield) of a material with a boiling point of 158-159° at 4 mm, which is characteristic of tetrabutoxydisilanemethane.

Found %: C 64.68, 64.74; H 12.89, 13.03.
 $C_{17}H_{40}OSi_2$ Calculated %: C 64.49; H 12.74.

Preparation of tetrabutylidihydroxydisilanemethane. To 75 ml of a 10% alcoholic solution of sodium hydroxide was added 23 g of tetrabutoxydisilanemethane. The mixture was heated to boiling for 6 hours. After evolution of hydrogen had ceased, the reaction mixture was cooled to room temperature, and 100 ml of petroleum ether and then 200 ml of water were added. The ether layer was washed with water to a neutral reaction, dried, and distilled. During distillation, part of the product condensed. There was obtained 8 g (32.9% yield) of a material with a boiling point of 185-189° at 5 mm, which is characteristic of tetrabutylidihydroxydisilanemethane.

Found %: C 61.80, 61.74; H 12.28, 12.19.
 $C_{17}H_{40}O_2Si_2$ Calculated %: C 61.39; H 12.12.

Preparation of bis(tetrabutylidisilanemethane)cyclodioxide. 20 g of tetrabutylidihydroxydisilanemethane was boiled with 50 ml of 40% hydrobromic acid for 10 hours, after which the mixture was cooled to room temperature, the product extracted with ether, neutralized with soda, washed, dried, and distilled. There was obtained, after a second distillation over metallic sodium, 12 g (63.5% yield) of a material with a boiling point of 214-216° at 1 mm, which is characteristic of bis(tetrabutylidisilanemethane)cyclodioxide.

Found %: C 64.93, 64.93; H 12.15, 12.17.
 $C_{24}H_{56}O_2Si_4$ Calculated %: C 64.90; H 12.18.

Molecular weight: found, 618 and 621; calculated for $C_{24}H_{56}O_2Si_4$, 629.

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SYNTHESIS OF γ -HYDROXYALKYLAMINONITRILES

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(Presented by Academician I. N. Nazarov, May 3, 1956)

Hydroxyalkylamino acids are of interest not only from the theoretical point of view as compounds containing simultaneously three different functional groups, but also as potentially physiologically active substances.

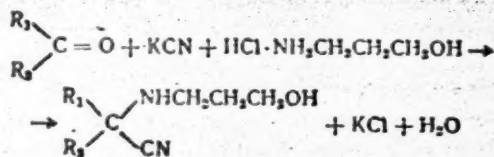
In a series of works published in 1925-1932, A. I. Kiprianov and co-workers described a practicable method of synthesis and the properties of representatives of this unusual class of organic substances; they prepared about 25 compounds in the β -hydroxyalkylamino acid series by the reaction of ethylene oxide and its homologs with esters of different α -amino acids and by the application of the Zelinsky-Stadnikov reaction to amino alcohols (ethanolamine, etc). The literature on hydroxyalkylamino acids is very limited and is mainly confined to a few works devoted to the synthesis of β -hydroxyalkylamino acids [2,8].

As regards γ -hydroxyalkylamino acids, although they are close to certain natural physiologically active substances (ecgonine) and in spite of the synthesis in very low yield by McElvain in 1924 of one of the compounds of this series, the benzoate of methyl- γ -hydroxypropylaminopropionic ester, by the action of trimethylene chlorohydrin on an ester of β -methylaminopropionic acid, up to the present time nothing is known about them and a convenient method for their synthesis has not been developed.

Moreover, A. I. Kiprianov [4] and B. A. Rashkovan [5] did not succeed in obtaining the expected γ -hydroxyalkylaminonitriles and the corresponding acids by the application of the method of Zelinsky and Stadnikov to γ -hydroxypropylamine. Thus, an apparent simple and easily practicable method for their synthesis proved to be a failure.

Wanting to explain the reasons for the lack of success of the above-mentioned investigators, we decided to investigate in greater detail the cyanohydrin method in its application to γ -hydroxypropylamine with the aim of finding favorable conditions for carrying it out. It was also stimulating to us that upon critical consideration of the mechanisms of the reaction involved in the cyanohydrin method of synthesis of aminonitriles proposed by various authors [6], among them B. A. Rashkovan [5], we were unable to discover any reason why γ -hydroxypropylamine should not enter into a similar reaction with carbonyl compounds and hydrocyanic acid.

Actually, by carrying out the Zelinsky-Stadnikov reaction of γ -hydroxypropylamine and potassium cyanide with benzaldehyde, cyclohexanone, acetone, and *n*-butyraldehyde we obtained under suitably mild conditions γ -hydroxyalkylaminonitriles according to the equation:



*The structure given by McElvain in the reference is γ -(methyl- β -carbo-ethoxy-ethyl)aminopropyl benzoate-Publisher.

Only in the case of the condensation in which formaldehyde was used as the carbonyl compound were we unsuccessful in isolating from the reaction products γ -hydroxypropylaminoacetonitrile and the corresponding acid; this was apparently due to their high water solubility which prevented isolation and purification. It should be noted that A. I. Kiprianov and B. A. Rashkovan were also unsuccessful in isolating individual reaction products from a similar condensation with formaldehyde, but 2-phenyltetrahydrooxazine was obtained from the condensation with benzaldehyde.

The formation of this heterocyclic compound can be visualized as proceeding either by means of the direct interaction of the amino alcohol and the carbonyl compound with the splitting out of a molecule of water, for example as observed by Kohn [7] during the condensation of diacetonealkamine [4-methyl-4-amino-2-pentanol] with aldehydes, or from a secondary reaction - the splitting out of hydrocyanic acid from the already formed γ -hydroxyalkylaminonitrile.

In the present investigation we showed that, in alkaline medium, γ -hydroxyalkylaminonitriles easily split out hydrogen cyanide, and are converted thereby into derivatives of tetrahydrooxazine. This same thing was observed in acid medium by means of the action of a solution of silver nitrate. We also observed a similar effect in the β -hydroxyalkylamino acid series [8]. Since B. A. Rashkovan did not avoid the use of an alkaline medium during the isolation of the products of the condensation of γ -hydroxypropylamine hydrochloride with potassium cyanide and benzaldehyde, naturally a secondary reaction proceeded under these conditions with the splitting out of the elements of hydrocyanic acid from the γ -hydroxyalkylaminonitrile with the formation of a derivative of tetrahydrooxazine.

This was confirmed by the almost quantitative formation of 2-phenyltetrahydrooxazine-1,3, described by B. A. Rashkovan, by the action of alkali on the (γ -hydroxypropylamino)-phenylacetonitrile hydrochloride prepared by us.

EXPERIMENTAL

γ -Hydroxypropylamino-phenylacetonitrile (hydrochloride). To 7.5 g (0.1 mole) of γ -hydroxypropylamine, previously neutralized with hydrochloric acid (1:1), was added a solution of 12 ml of freshly distilled benzaldehyde in 80 ml of alcohol. A solution of 6.5 g (0.1 mole) of potassium cyanide in 40 ml of water was then added in small portions. Evolution of heat was observed upon mixing of the reacting materials. After a day, the alcohol was distilled off under vacuum, and the reaction product was extracted with ether. The ether solution was dried with anhydrous sodium sulfate, and, after removal of the latter, dry hydrogen chloride was passed into the filtrate while cooling with ice water. The crystalline precipitate was washed with absolute ether and recrystallized from a mixture of alcohol and ether. The γ -hydroxypropylaminophenylacetonitrile hydrochloride was a white crystalline (plates) material, readily soluble in water (with an acid reaction to litmus) and alcohol, and insoluble in ether and benzene. After heating with a solution of alkali, the aqueous solution gave a positive reaction for cyanide ion. The yield was 14.8 g (65% of theoretical). M.p. 117-119° (with decomposition) (from an alcohol-ether mixture).

Found %: N 12.43; Cl 15.58; CN 11.43.

$C_{11}H_{15}ON(CN) \cdot HCl$ Calculated %: N 12.35; Cl 15.64; CN 11.47.

1-(γ -Hydroxypropylamino)-1-phenylacetic acid. 2.0 g γ -hydroxypropylaminoacetonitrile hydrochloride was hydrolyzed with hydrochloric acid on a water bath. At the conclusion of the hydrolysis, the hydrochloric acid solution was evaporated to dryness. The dry residue was treated with absolute alcohol to separate the ammonium chloride. The alcoholic solution was evaporated, the residue dissolved in a small amount of water, and pyridine was added dropwise to this aqueous solution to a neutral reaction toward litmus. The liberated free alkamino [hydroxyalkylamino] acid was filtered, washed with alcohol and ether, and dried under vacuum. The 1-(γ -hydroxypropylamino)-1-phenylacetic acid was a white crystalline material, soluble in water with a neutral reaction to litmus, and insoluble in alcohol and ether. The yield was 0.5 g (27% of theoretical). M.p. 184-186°.

Found %: N 6.57.

$C_{11}H_{15}O_2N$ Calculated %: N 6.69.

2-Phenyltetrahydrooxazine-1,3. 7 g of γ -hydroxypropylaminophenylacetonitrile hydrochloride was dissolved in a small amount of water and heated with 40 ml of a 10% solution of KOH for 15 minutes. The solution obtained was extracted with ether. The ethereal extract was dried with potassium carbonate, and the ether distilled off. The only residue was distilled under vacuum. The yield was 4 g (79% of theoretical). B.p. 175-177°/30 mm. A mixture of equimolecular quantities of 2-phenyltetrahydrooxazine and picric acid in alcohol solution gave the picrate with a m.p. of 130-131°.

1-(γ -Hydroxypropylamino)-hexahydrobenzonitrile. To 7.5 g (0.1 mole) of γ -hydroxypropylamine, previously neutralized with hydrochloric acid (1:1), was added a solution of 12 ml of freshly distilled cyclohexanone in 80 ml of alcohol. A solution of 6.5 g (0.1 mole) of potassium cyanide in 60 ml of water was then added in small portions. A rather considerable evolution of heat was observed upon mixing of the reactant materials. After two days, the alcohol was distilled under vacuum, and the liberated oily layer was extracted with ether. The ethereal solution was dried with anhydrous sodium sulfate, and a large part of the ether was distilled. The crystalline precipitate was filtered and dried under vacuum. The 1-(γ -hydroxypropylamino)-hexahydrobenzonitrile was a white crystalline (needles) material, readily soluble in water. Upon the addition of silver nitrate to the aqueous alcoholic solution of the aminonitrile in an acid medium, a precipitate of silver cyanide was formed. A solution of the material gave a positive reaction for cyanide ion after heating with alkali. The yield was 14.4 g (79% of theoretical). M.p. 87-88° (from gasoline).

Found %: N 15.22.
 $C_6H_{14}ON(CN)$. Calculated %: N 15.29.

The hydrochloride was obtained by passing dry hydrogen chloride into a solution of 2 g of the alkaminonitrile [hydroxyalkylaminonitrile] in 120 ml of absolute ether. The yield was almost quantitative. The hydrochloride dissolved readily in water (with an acid reaction to litmus) and in alcohol, and was insoluble in ether. M.p. 128° (from alcohol-ether mixture).

Found %: Cl 16.05; CN 11.76.
 $C_6H_{12}ON(CN) \cdot HCl$. Calculated %: Cl 16.14; CN 11.84.

1-(γ -Hydroxypropylamino)-isobutyronitrile (hydrochloride) was prepared similarly to the preceding alkaminonitrile. Acetone (10 ml) was used as the carbonyl compound in the condensation reaction. The 1-(γ -hydroxypropylamino)-isobutyronitrile was a white crystalline material, readily soluble in alcohol and in water with an acid reaction to litmus, and insoluble in ether and benzene. The aqueous solution gave a positive reaction for cyanide ion after the addition of alkali. The yield was 4.1 g (23% of theoretical). M.p. 102-104° (from alcohol-ether mixture).

Found %: N 15.62; Cl 19.75; CN 14.48.
 $C_6H_{14}ON(CN) \cdot HCl$. Calculated %: N 15.68; Cl 19.85; CN 14.56.

1-(γ -Hydroxypropylamino)-valeronitrile (hydrochloride). This compound was prepared similarly to the preceding using n-butyraldehyde (a solution of 10 ml of aldehyde in 60 ml of alcohol) as the carbonyl compound. The 1-(γ -hydroxypropylamino)-valeronitrile was a white crystalline material, readily soluble in water (with an acid reaction to litmus) and in alcohol, and insoluble in ether and benzene. The aqueous solution gave a positive reaction for cyanide ion after heating with alkali solutions. The yield was 10.8 g (56% of theoretical). M.p. 142-144° (with decomposition) (from absolute alcohol).

Found %: N 14.73; Cl 18.28; CN 13.41.
 $C_7H_{16}ON(CN) \cdot HCl$. Calculated %: N 14.54; Cl 18.40; CN 13.50.

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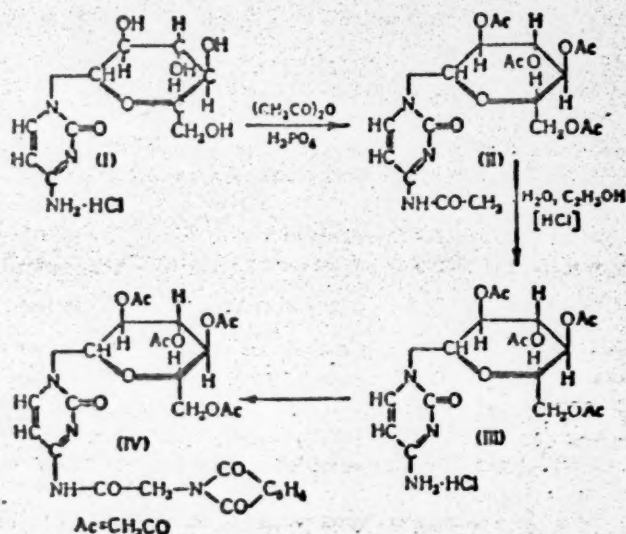
AMINOACYL DERIVATIVES OF NUCLEOSIDES. SYNTHESIS OF N₆-AMINOACYL DERIVATIVES OF 3-β-D-GLUCOPYRANOSYLCYTOSINE

Z. A. Shabarova and M. A. Prokofyev

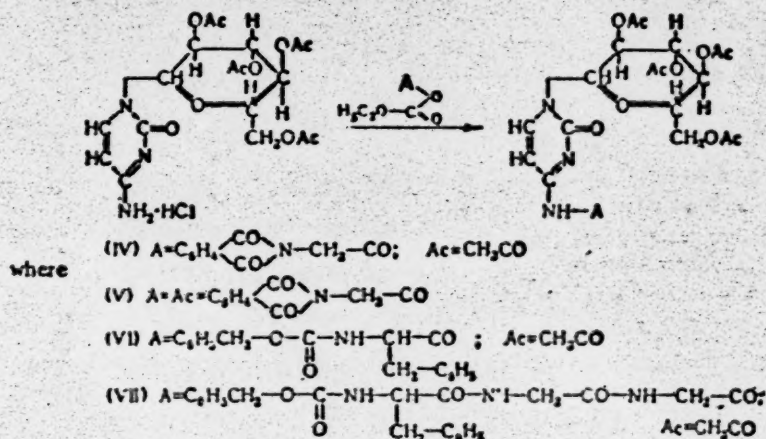
(Presented by Academician A. N. Nesmeyanov, February 13, 1956)

Polyaminoacyl derivatives of nucleosides and nucleotides, in particular those which have a polyaminoacyl (polypeptide or peptidodiketopiperazine) group, bonded to the amino group of the nitrogen bases (cytosine, 5-methylcytosine, adenine, guanine), have an important significance in the chemistry of nucleoproteins. The question of the significance of compounds of such type as models of one of the possible forms of the bonds of nucleic acid and albumin in nucleoproteins [1] has been discussed in the literature.

We undertook an investigation in this field in order to develop methods of synthesis of aminoacyl derivatives of nucleosides and to study the properties of the compounds obtained. The present work communicates the results of an investigation on the synthesis of N₆-aminoacyl derivatives of 3-β-d-glucopyranosylcytosine. 3-β-d-Glucopyranosylcytosine hydrochloride (I), prepared by the method of Hilbert and co-workers, somewhat modified, from 2,6-diethoxypyrimidine and tetraacetylthiomoglucose [2], served as the starting material for the syntheses. In contrast to the 4(6)-aminopyrimidines studied earlier by us [3], the amino group of 3-β-d-glucopyranosylcytosine reacted rather readily with acetic anhydride, phthalylglycyl chloride, and, of particular importance, with mixed anhydrides of amino acids. Upon heating (I) with acetic anhydride at 50° in the presence of H₃PO₄, the pentaacetyl derivative (II) was formed, which, however, easily lost one acyl group on heating with 96% alcohol in the presence of HCl, being converted to the tetraacetyl derivative (III). By the reaction of (III) with phthalylglycyl chloride, it was shown that the amino group of a cytosine nucleoside can be easily acylated by the acid chloride of an amino acid with the formation of an N₆-aminoacyltetraacetyl-3-β-d-glucopyranosylcytosine (IV).



Among the 4(6)-aminopyrimidines, the amino group reacted with a mixed anhydride of an amino acid only in the case of cyanmethine [3], in which the basicity of the amino group is increased. With 3- β -D-glucopyranosylcytosine, acylation of the amino group with a mixed anhydride of an amino acid was accomplished easily. By the action on (I) of the mixed anhydride of phthalylglycine and diethyl carbonate, the pentaacetylglucosyl derivative (V) was obtained in good yield. Reaction of this same anhydride with (III) led to the formation of the N_6 -aminoacyl derivative (IV), which was also prepared from (III) and phthalylglycyl chloride. The mixed anhydride of phenylalanine and diethyl carbonate reacted analogously with (III); in this instance, N_6 -(phenylalanyl)tetraacetyl-3- β -D-glucopyranosylcytosine (VI) was formed. N_6 -(phenylalanyl)glycylglycyltetraacetyl-3- β -D-glucopyranosylcytosine (VII) was formed by the reaction of (III) with the mixed anhydride of phenylalanylglycylglycine.



EXPERIMENTAL

1. Preparation of pentaacetyl-3- β -D-glucopyranosylcytosine (II). To 1 g of (I) was added 4 ml of acetic anhydride and several drops of H_2PO_4 . The reaction mixture was heated at 50° for 4 hours and poured onto ice. The oil which separated out in the cold crystallized. The yield of (II) was 1.4 g (90%). M.p. 225° (from 80% alcohol). UV absorption in 96% alcohol: λ_{max} 251; 300 m μ (log ϵ 2.6; 2.2). Literature data for (II): m.p. 225° [2].

2. Preparation of 3- β -D-tetraacetylglucopyranosylcytosine hydrochloride (III). A suspension of 1 g of (II) in 20 ml of 96% alcohol and 0.3 ml of concentrated HCl was heated for 30 minutes on a water bath. The solution was evaporated under vacuum. The residual oil was treated with 10 ml of absolute alcohol. The precipitate formed in the cold was filtered and purified by reprecipitation from alcohol solution by ether. The yield of (III) was 0.7 g (65%). M.p. 201°. The material for analysis was dried in a vacuum over P_2O_5 at 110° for 10 hours.

Found %: C 42.15; H 5.50; N 8.25.

$C_{18}H_{24}O_{14}N_2Cl \cdot 2H_2O$. Calculated %: C 42.10; H 5.45; N 8.19.

UV absorption in 96% alcohol: λ_{max} 275 m μ (log ϵ 2.4).

3. Preparation of N_6 -(phthalylglycyl)tetraacetyl-3- β -D-glucopyranosylcytosine (V). A solution of 0.2 g of (III) in 10 ml of dioxane and 0.1 ml of tributylamine was heated with 6.1 g of phthalylglycyl chloride at 50° for 4 hours. After evaporation under vacuum to 1/3 the volume, the reaction mixture was poured onto ice. The precipitate was washed with ice water. The yield of (IV) was 0.12 g (50%). The material was purified by reprecipitation from benzene by petroleum ether. It decomposed at 152-153°.

Found %: C 53.35; H 4.27; N 9.10.

$C_{23}H_{25}O_{13}N_4$. Calculated %: C 53.50; H 4.46; N 8.92.

UV absorption in 96% alcohol: γ_{\max} 240; 298 m μ (log ϵ 2.0; 2.4).

4. Preparation of penta(phthalylglycyl)-3- β -D-glucopyranosylcytosine (V). To a solution of 0.34 g of phthalylglycine in 5 ml of chloroform and 0.4 ml of tributylamine, cooled to 0°, was added 0.016 ml of ethyl chlorocarbonate. The solution was kept at 0° for 30 minutes, and then a solution of 0.1 g of (I) in 0.5 ml of water containing 0.013 g NaOH was added to it. The reaction mixture was cooled in a vacuum for 10 minutes, and then remained in the cold for 3 hours. After evaporation under vacuum, 10 g of crushed ice was added to the residue. The copious precipitate of (V) was filtered and washed with water and alcohol. For purification, (V) was dissolved in 25 ml of chloroform, and the solution was evaporated to 1/3 its volume. After cooling, the precipitate was filtered. The yield was 0.15 g (40%). *l.p.* 239-240°.

Found %: C 60.10; H 3.31; N 9.23.
 $C_{66}H_{46}O_{21}N_6$. Calculated %: C 59.60; H 3.31; N 9.27.

UV absorption in 96% alcohol: λ_{\max} 297 m μ (log ϵ 2.5).

5. Preparation of (IV) from (III) and the mixed anhydride of phthalylglycine. To a solution of 0.08 g of phthalylglycine in 4 ml of chloroform and 0.1 ml of tributylamine, cooled to 0°, was added 0.04 ml of ethyl chlorocarbonate. The reaction mixture was held at 0° for 15 minutes, and then a solution of 0.2 g of (III) in 4 ml of dioxane and 0.1 ml of tributylamine was added to it. The solution was placed in a vacuum for 30 minutes, and then it was held in the cold for 1 day. After evaporation under vacuum, 5 g of crushed ice was added to the oil. The precipitate was filtered and washed with 0.1 N NaOH, 0.1 N HCl, and water. The yield of (IV) was 0.15 g (60%). The material was purified by reprecipitation from benzene by petroleum ether. It decomposed at 152-154°. A mixed melting point with (IV) from experiment 3 did not show a lowering of the decomposition temperature.

6. Preparation of N₆-(phenylalanyl)tetraacetyl-3- β -D-glucopyranosylcytosine (VI). This compound was prepared analogously to that described above from the mixed anhydride of phenylalanine and (II) in dioxane. The yield of (VI) was 55%. It decomposed at 143-145° (from benzene-petroleum ether mixture).

Found %: C 58.35; H 5.44; N 7.77.
 $C_{55}H_{42}O_{15}N_6$. Calculated %: C 58.17; H 5.26; N 7.75.

UV absorption in 96% alcohol: λ_{\max} 250; 300 m μ (log ϵ 3.3; 2.9).

7. Preparation of N₆-(phenylalanylglycylglycyl)tetraacetyl-3- β -D-glucopyranosylcytosine (VII). To a solution of 0.12 g of phenylalanylglycylglycine in 5 ml of dioxane and 0.11 ml of tributylamine at 10° was added 0.03 ml of ethyl chlorocarbonate and, at this same temperature over a 30-minute period, 0.15 g of (IV) in 0.5 ml of water containing 0.012 g of NaOH. The reaction mixture was placed in a vacuum for 30 minutes, and then held for 1 day at 10°. After evaporation under vacuum, ether was added to the residue. The oil was separated, treated several times with ether, and poured onto ice. The precipitate was washed with ice water, 0.1 N NaOH, and 0.1 N HCl, and reprecipitated from alcohol by ether. The yield of (VII) was 0.1 g (42%). *M.p.* 139-140°. Before analysis, the material was dried under vacuum over P_2O_5 at 75° for 20 hours.

Found %: C 54.68; H 5.47; N 9.65.
 $C_{55}H_{44}O_{15}N_6 \cdot H_2O$. Calculated %: C 54.80; H 5.38; N 9.83.

UV absorption in 96% alcohol: λ_{\max} 250; 301 m μ (log ϵ 2.2; 1.8).

We consider it our pleasant duty to express our appreciation to D. A. Morozova, who kindly supplied us with the phenylalanylglycylglycine.

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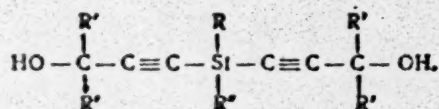
INVESTIGATIONS IN THE FIELD OF THE SYNTHESIS AND TRANSFORMATIONS OF UNSATURATED ORGANOSILICON COMPOUNDS. SYNTHESIS OF ORGANOSILICON GLYCOLS OF THE DIACETYLENE SERIES

M. F. Shostakovsky, I. A. Shikhiev and N. V. Komarov

(Presented by Academician B. A. Kazansky, January 14, 1956)

In our previous investigations, we studied the reactivity of organosilicon compounds containing hydroxyl groups [1].

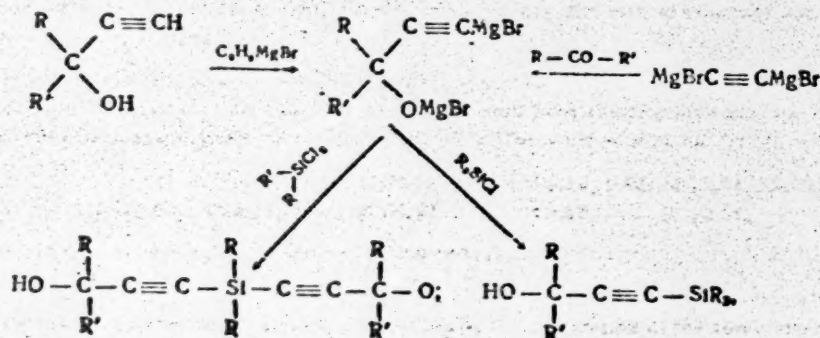
With the aim of furthering the development of our investigations in the field of the synthesis and transformations of hydroxyl-containing organosilicon compounds, we decided to synthesize diacetylenic organosilicon glycols of the following general structure:



For the preparation of the indicated compounds, we used the organomagnesium synthesis of Zh. I. Iotsich [2], which is well known in organic chemistry.

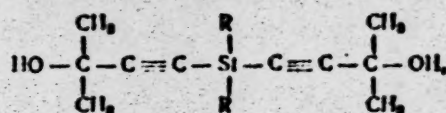
As is well known, haloalkyls [3] and chlorosilanes [4] react readily with organomagnesium compounds.

For the synthesis of the organosilicon glycols of the diacetylene series (or for the preparation of organosilicon alcohols of the acetylene series), we studied the reaction of dialkyldichlorosilanes (or of trialkylchlorosilanes) with dimagnesiumdibromodimethylacetylenylcarbinol. This reaction can be represented in general terms as follows:



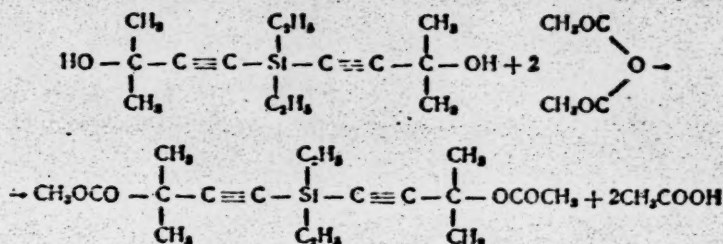
where R or R' can be H, CH₃, C₂H₅, CH₂=CH-, aryl, etc.

This means was used to prepare three representatives of the above-mentioned organosilicon glycols of the following structures:



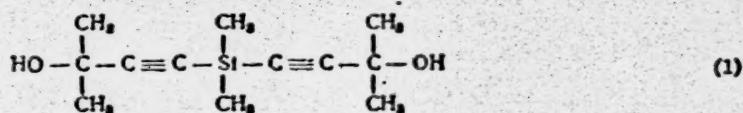
where R is CH_3 , C_2H_5 , and C_3H_7 .

The presence of two hydroxyl groups was demonstrated by the preparation of the acetyl derivative of di(dimethylacetylenyl- γ -hydroxy)-diethylsilane according to the following reaction:



EXPERIMENTAL

Synthesis of Di(dimethylacetylenyl- γ -hydroxy)dimethylsilane.



84 g (1 mole) of dimethylacetylenylcarbinol in 100 ml of absolute ether was added to the constantly stirred Grignard reagent (prepared from 48g Mg and 220g $\text{C}_2\text{H}_5\text{Br}$) while cooling with ice water. The mixture was stirred for 2 hours while cooling with ice water, and 65 g (0.5 mole) of dimethyldichlorosilane was then added. The reaction mixture was allowed to stand overnight. On the following day, the viscous complex was decomposed with hydrochloric acid (10-15%) while cooling.

The aqueous layer was separated from the ether layer, which was then dried over sodium sulfate. The ether was distilled off; from the residue, after two-fold recrystallization from absolute benzene, was isolated 72 g of product in the form of acicular crystals with a m.p. of 80-82°. The yield was 64.3%.

Found %: C 64.57, 64.55; H 9.16, 9.06; Si 12.54, 12.64.
 $\text{C}_{12}\text{H}_{22}\text{SiO}_2$. Calculated %: C 64.24; H 8.98; Si 12.50.

The analytical data correspond to the diacetylenic glycol (1).

Two other syntheses were carried out by this same method using diethyl- and dipropyldichlorosilane and dimagnesiumdibromodimethylacetylenylcarbinol and leading to the preparation of the two corresponding organosilicon diacetylenic glycols, di-(dimethylacetylenyl- γ -hydroxy)diethyl- and di(dimethylacetylenyl- γ -hydroxy)dipropylsilane. The elemental compositions and the melting points of these glycols are presented in Table 1.

Synthesis of Di(dimethylacetylenyl- γ -acetoxy)diethylsilane

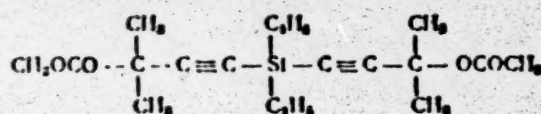


TABLE 1

General Characterization of the Organosilicon Diacetylenic Glycols

Prep. No.	Formula	M.p., °C	Elemental analysis, %						Yield, %
			C		Si		H		
			found	calc.	found	calc.	found	calc.	
1	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \\ \quad \quad \\ \text{HC}-\text{C}-\text{C}\equiv\text{C}-\text{N}-\text{C}\equiv\text{C}-\text{C}-\text{OH} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	80-82	64.57 64.55	64.24	12.54 12.64	12.50	9.16 9.06	8.98	64.3
2	$\begin{array}{c} \text{CH}_3 \quad \text{C}_2\text{H}_5 \quad \text{CH}_3 \\ \quad \quad \\ \text{HO}-\text{C}-\text{C}\equiv\text{C}-\text{Si}-\text{C}\equiv\text{C}-\text{C}-\text{OH} \\ \quad \quad \\ \text{CH}_3 \quad \text{C}_2\text{H}_5 \quad \text{CH}_3 \end{array}$	76-78	66.34 66.47	66.61	11.61 11.70	11.11	9.63 9.47	9.58	55
3	$\begin{array}{c} \text{CH}_3 \quad \text{C}_2\text{H}_5 \quad \text{CH}_3 \\ \quad \quad \\ \text{HO}-\text{C}-\text{C}\equiv\text{C}-\text{N}-\text{C}\equiv\text{C}-\text{C}-\text{OH} \\ \quad \quad \\ \text{CH}_3 \quad \text{CH}_3 \quad \text{CH}_3 \end{array}$	70-71	65.48 68.52	68.51	10.11 10.03	10.06	9.98 10.01	10.01	48

To 25.3 g (0.1 mole) of di(dimethylacetylenyl- γ -hydroxy)diethylsilane was added 20.4 g (0.2 mole) of acetic anhydride. The mixture was heated at 70° for 8 hours with constant stirring, and then allowed to stand overnight. The acetic acid was distilled off; from the residue, after two-fold distillation, was isolated 20.6 g (61.0% yield) of a material boiling at 104-141°/3 mm; n_D^{20} 1.4639; d_4^{20} 0.9675.

Found %: MR_D 95.97.

$\text{C}_{18}\text{H}_{22}\text{SiO}_4$. Calculated %: MR_D 95.42.

Found %: C 64.10, 63.92; H 8.64, 8.69.

$\text{C}_{18}\text{H}_{22}\text{SiO}_4$. Calculated %: C 64.24; H 8.39.

These data corresponds to di(dimethylacetylenyl- γ -hydroxyacetoxy)diethylsilane.

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SYNTHESIS OF HIGHER ALIPHATIC ALCOHOLS FROM CO AND H₂

A. N. Bashkirov, Yu. B. Kagan and L. I. Zvezdkina

(Presented by Academician A. A. Balandin, January 23, 1956)

From the moment of their discovery the development of catalytic syntheses from carbon monoxide and hydrogen has been along two primary directions; on the one hand the syntheses of hydrocarbons were developed, and on the other hand the syntheses of alcohols.

As is known, the first of these directions led to the discovery of many new catalysts and the creation of a number of processes which permitted obtaining various hydrocarbons, beginning with methane and ending in a high-molecular paraffin. The synthesis of liquid, predominantly unbranched, aliphatic hydrocarbons from CO and H₂ was accomplished on an industrial scale [1,2].

Much poorer results were achieved in the field of synthesizing alcohols from CO and H₂. Only the synthesis of methyl alcohol is currently achieved on a broad commercial scale. The synthesis of isobutyl oil, which has received fairly extensive study, gives a product that usually contains over 50% of methanol, about 12% isobutyl alcohol and several percent of other higher alcohols, and in essence the process is one of synthesizing methanol with a certain amount of higher alcohols [1]. The pilot plant studies made in the past of the German "synol process" gave a mixture of products, composed of nearly equal amounts of hydrocarbons and higher aliphatic alcohols with a small amount of other oxygen-containing organic compounds [1,3].

As a result, in contrast to the synthesis of the higher hydrocarbons, not only has the synthesis of the higher alcohols not been realized on an industrial scale, but even its development has been unsuccessful up to now.

The discovery of a method for synthesizing the higher aliphatic alcohols from CO and H₂ with a fairly high yield of the desired product has both scientific and practical interest.

With the purpose in mind of achieving such a process we developed and investigated in the synthesis a number of differently activated iron catalysts, operating in the temperature range from 150 to 170°. The catalytic hydrogenation of carbon monoxide under these conditions leads to obtaining liquid products that consist of 80-90% of oxygen-containing organic compounds. The fraction of alcohols in these liquid synthesis products can be as high as 75-80%. Together with the alcohols about 5-10% of carbonyl compounds (chiefly aldehydes) is formed, the further hydrogenation of which, similar to that used in the "oxo process" [4], permits increasing the amount of alcohols in the reaction products up to 85-90%.

In the wide fraction, boiling in the range 105-200°, the amount of organic oxygen-containing compounds approaches 100%. The yield of liquid synthesis products (excluding water) attains a value of 170 ml/m³ (NTP) of treated gas (CO + 2H₂). The output of the catalysts in the experiments where the return gas was recirculated, using a recirculation coefficient of 7, was as high as 1.1 liters of liquid product per liter of catalyst per day, which corresponds to complete conversion of the carbon monoxide at a space velocity of 300 hr.⁻¹ (against 150 hr.⁻¹ in the synol process [5]). Depending on the catalyst composition and synthesis conditions the fractional composition of the obtained products can show some variation.

For the syntheses where a gas ratio H₂:CO = 2:1 was used the following distribution of the alcohols was characteristic: the methyl alcohol fraction represents about 10% of the total amount of obtained alcohols, the fraction composed of the C₂, C₃ and C₄ alcohols represents about 50%, and the amount of alcohols higher than C₄ reaches 40%.

TABLE 1
Characteristics of Isolated Alcohols

Alcohol	B.p., °C/mm		Hydroxyl number		n _D ²⁰		M.p. of phenylurethan, °C		Elementary analysis results in %																	
									alcohol				phenylurethan													
	found	literature [6]	found	calcd.	found	literature [10]	found				calcd.				found				calcd.							
							C	H	O	C	H	C	H	N	C	H	N	C	H	N						
CH ₃ OH	64.6-65	64.7	1703	1753	1.3313	1.3290(?)			37.39	12.51	37.50	12.50														
C ₂ H ₅ OH	78.2-78.8	78.3	1218	1220	1.3627	1.3623(?)			—	—	—	—														
C ₃ H ₇ OH	96.5-97.5	97.2	905	934	1.3849	1.3849(?)			52.02	13.03	52.17	13.04														
C ₄ H ₉ OH	116.9-117.1	117.0	762	758	1.3992	1.3993(?)	58.1-58.5°	60	64.85	13.52	64.85	13.51	68.48	7.73	7.19	68.39	7.77	7.25								
C ₅ H ₁₁ OH	130.5-137.1	137.8	634	637	1.4099	1.4099(?)	48-46.4°	46	68.17	13.67	68.16	13.63	69.60	8.24	6.74	69.56	8.21	6.76								
C ₆ H ₁₃ OH	150.4-157.4	157.1	533	550	1.4179	1.4181(?)	41-41.3°	41	70.47	13.69	70.58	13.72	70.60	8.58	6.38	70.58	8.59	6.33								
C ₇ H ₁₅ OH	75-77/10	74.7/10	487	484	1.4250	1.4250(?)	57°	59	72.28	13.80	72.41	13.79	71.52	9.00	5.94	71.48	8.93	5.95								
C ₈ H ₁₇ OH	87-89/10	87.7/10	427	432	1.4295	1.4304(?)			73.68	13.89	73.84	13.84														
C ₉ H ₁₉ OH	99-102/10	99.7/10	380	369	1.4339	1.4338(?)			74.96	13.86	75.00	13.89														
C ₁₀ H ₂₁ OH	110.1-115/10	111.4/10	359	355	1.4362	1.4366(?)			75.95	13.91	75.95	13.92														

* The mixed melting points with the phenylurethans of the corresponding alcohols failed to be depressed.

The following alcohols were isolated from the obtained synthetic products and were identified by their physical constants, elementary analysis data, hydroxyl numbers, and in some cases, by the melting points and analysis of their phenylurethans: methyl, ethyl, n-propyl, n-butyl, n-amyl, n-hexyl, n-heptyl, n-octyl, n-nonyl and n-decyl.

These alcohols constitute the major portion of the investigated product. The data characterizing the isolated alcohols are collected in Table 1.

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MOLECULAR COMPLEXES OF NITROSYL CHLORIDE

E. V. Genkina, A. I. Finkel'shtein and A. A. Artemyev

(Presented by Academician L. L. Kurnyants, January 14, 1956)

A number of papers by various authors have been devoted to a study of the absorption spectra of nitrosyl chloride in the visible and ultraviolet regions [1-6]. These authors established the presence of a number of broad bands in the absorption spectrum of gaseous nitrosyl chloride, having absorption maxima at wavelengths corresponding to 601.7; 475; 440; 335; 197; 150 m μ . In addition to these broad bands there was also shown the presence of six narrow bands in the 530-630 m μ region, having absorption maxima at wavelengths 643.1; 615.8; 587.9; 561.2; 549.5; 538.5 m μ of the fine structure indicated by Kistiakowsky [3] in the 400-450 m μ region of the spectrum for gaseous nitrosyl chloride was not supported in later studies [5,6].

The nature of the bands corresponding to wavelengths below 530 m μ is determined [4] by primary dissociation of the nitrosyl chloride molecule



The interpretation of the bands in the 530-630 m μ region is less clearly defined. Apparently [5] predissociation takes place here, leading to cleavage of the molecule.

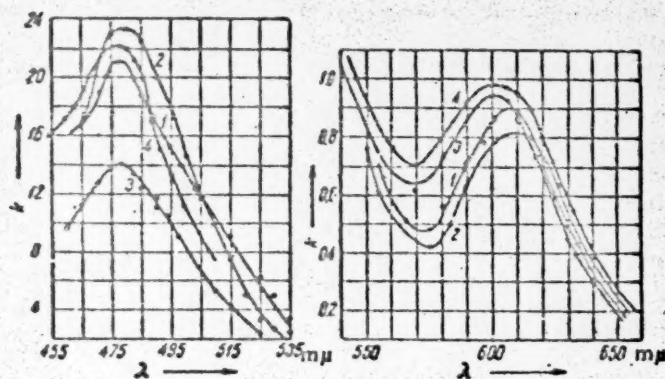


Fig. 1. Absorption curves in the visible region of NOCl solutions in nonpolar inert solvents. 1) In cyclohexane; 2) In heptane; 3) In CCl₄; 4) In cyclooctane.

In this paper we give our study results on the absorption spectra of nitrosyl chloride in a number of organic solvents.

The results that we obtained (Figs. 1-4) show very clearly that the studied compounds exert a variable influence on the absorption spectrum of nitrosyl chloride. In this connection it is expedient to divide them into three groups. The first group contains the nonpolar solvents (cyclohexane, cyclooctane, n-heptane, carbon

tetrachloride) (Fig. 1); the substances showing easy polarization of the benzene ring should be classified as belonging to the second group (benzene, ethylbenzene, benzyl chloride) (Fig. 2); the third group contains the polar aliphatic halides (ethyl bromide, dichloroethane, n-butyl bromide, n-heptyl bromide) (Fig. 3).

The absorption spectra in the visible region for the solutions of nitrosyl chloride in the enumerated compounds are plotted in Figs. 1-3, while the corresponding spectra in the ultraviolet region are plotted in Fig. 4. Our studies revealed that in nonpolar inert solvents the absorption curves of nitrosyl chloride solutions coincide with the absorption curves of gaseous NOCl, differing from the latter only in absolute value.

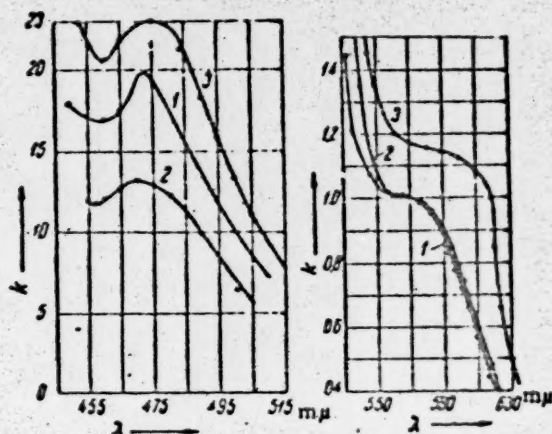
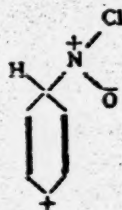


Fig. 2. Absorption curves in the visible region of NOCl solutions in benzene and some of its derivatives. 1) in benzene; 2) in benzyl chloride; 3) in ethylbenzene.

The absorption curves of NOCl solutions in ethyl bromide and dichloroethane are characterized by a shifting of the maximum toward the short wave portion of the spectrum. This apparently is associated with deformation of the electron cloud of the nitrosyl chloride molecule under the influence of the dipole molecules of the solvent. Heptyl bromide exerts a much smaller influence on the character of the nitrosyl chloride absorption curve.

The absorption curves of nitrosyl chloride solutions in benzene and some of its derivatives are characterized by some shifting of the maximum of the blue-green region toward the shorter wavelength portion of the spectrum, and in addition, by the complete deformation of the curve in the 600-610 mμ region, and instead of a maximum, the formation of only a slight inflection with subsequent rise. In this case it is possible that molecular compounds are formed as the result of unshared NOCl electrons reacting with the π -electrons of the benzene ring. Here it is possible to form an unstable complex having the structure:



similar to the structure proposed by A. L. Titov [7] for the complex of benzene with the NO₂ radical. Naturally, the formation of such a complex leads to redistribution of the electron density between its constituent atoms, which then appears as a change in the absorption curve of NOCl.

It is well known [8] that benzene is capable of forming complexes with inorganic substances that contain atoms with unshared electron pairs (AlCl_3 ; SbCl_5 ; AgClO_4 ; NbCl_5 ; AlBr_3).

The compounds that are formed here, failing to be stable, at the same time are also more reactive than is benzene itself, which is the result of certain difference in charge arising on the carbon atoms of the benzene ring due to conjugation with the complex-forming atom.

Of interest is the fact that the absorption curve of nitrosyl chloride in benzene solution for the blue-green region is located between the absorption curves for its corresponding solutions in ethylbenzene and benzyl chloride.

Apparently, this is not a chance phenomenon but instead is associated with the opposite character of the substituents: the electrophilic halogen atom in benzyl chloride and the electron-donor CH_3 group in ethylbenzene.

In the ultraviolet region the absorption maximum at $\lambda = 335 \text{ m}\mu$, corresponding to the absorption of gaseous nitrosyl chloride, appears only in the solvents of the first group. An inflection of the curve and a sharp increase in the absorption coefficient is observed in all of the other cases.

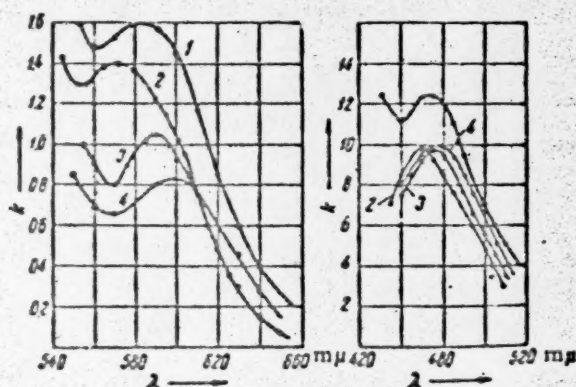


Fig. 3. Absorption curves in the visible region of NOCl solutions in some aliphatic chlorides. 1) In ethyl bromide; 2) in dichloroethane; 3) in *n*-butyl bromide; 4) in *n*-heptyl bromide.

The results that we obtained indicate that intermolecular reaction between nitrosyl chloride and the solvent is apparently due to dipole or polarization forces, which also leads to a greater polarization of the NOCl molecule and facilitates its dissociation by the mechanism proposed by G. L. Natanson [5].

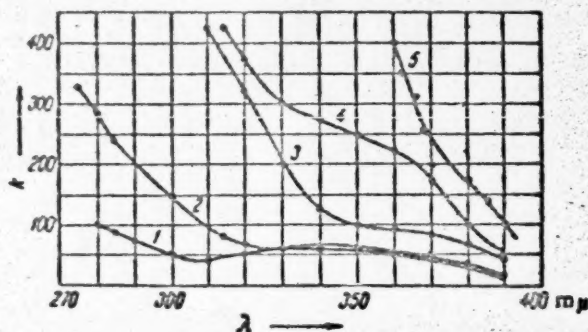


Fig. 4. Absorption curves in the ultraviolet region of NOCl solutions in a number of compounds. 1) In carbon tetrachloride; 2) in cyclohexane; 3) in dichloroethane; 4) in ethylbenzene; 5) in benzene.

The established absence of fine structure in the 500-600 m μ region can be explained as being due to a change in its state of aggregation when nitrosyl chloride enters the dissolved state.

We also observed a similar phenomenon (the disappearance of fine structure in the absorption spectrum) when we studied the solution of NO₂ in a number of hydrocarbons.

The change in the electronic structure of nitrosyl chloride under the influence of certain solvents, which is supported by dissimilarity in the absorption spectra of its solutions, is associated with the different behavior shown by the investigated compounds in the photochemical reaction with nitrosyl chloride.

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- [8] G. G. Gustavson, Ber., 11, 2151 (1878); J. Russ. Phys.-Chem. Soc., 10, 305 (1878); Ibid., 10, 390 (1878); Ibid., 22, 444 (1890); A. Rosenheim, W. Stellmann, Ber., 34, 3377 (1902); A. Hill, J. Am. Chem. Soc., 44, 1165, 1166 (1922); H. Fink and K. Niedeckler, Ber., 61, 1386 (1938).

DOUBLE SULFATES OF TITANIUM WITH AMMONIUM SULFATE

Ya. G. Goroshchenko

(Presented by Academician A. N. Frumkin, February 23, 1956)

It has been proposed that the double sulfates of titanium and ammonium can be used in the treatment of ilmenite concentrates for the purpose of removing iron and other impurities from the titanium [1]. Effective methods of decomposing a titanium-containing crude by fusion with ammonium sulfate and sulfuric acid are based on the formation of double sulfates. The properties of the simple titanium sulfates, on which a single harmonious viewpoint still fails to exist in the literature, can be indirectly judged by the properties of the double sulfates.

Rosenheim and Schutte [2] were the first to obtain the compound $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$. Mention of the compound $(\text{NH}_4)_2\text{Ti}(\text{SO}_4)_2$ is made in a number of literature references. However, up to now a systematic study of the double sulfates of titanium and ammonium has not been made. In our work they were studied by the preparative method. The formation of double salts was followed in a broad region of the $\text{TiO}_2 - \text{SO}_3 - (\text{NH}_4)_2\text{SO}_4 - \text{H}_2\text{O}$ system, both in aqueous solutions and in melts. All of the double sulfates detected in this system were isolated in the pure state. Their chemical composition was determined by chemical analysis.

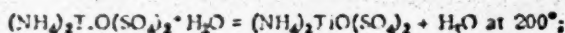
The double salt $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is obtained by mixing aqueous solutions of titanyl sulfate, containing sulfuric acid, and ammonium sulfate. The latter can also be added as a solid to the titanyl sulfate solution. The salt precipitates slowly. At room temperature its crystallization is complete only after 12-24 hours.

To obtain the pure salt the crystals, suction-filtered on a Buchner funnel, were first washed with 1:1 alcohol-water, then with 96% alcohol, and air-dried. Externally the $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is a white powder. The crystals are tetrahedrons or tetragonal tetrahedron. (see Fig. 1) with refractive index $N = 1.580 \pm 0.005$. The salt is readily soluble in water, its concentrated solutions are stable at room temperature, and from dilute solutions it precipitates as quadrivalent TiO_2 gel. The double salt is completely hydrolyzed when its aqueous solution is boiled. Hydrolysis of the salt yields a titanium dioxide that can be used as a pigment.

The solubility of $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ is lowered when ammonium sulfate and sulfuric acid are added to its aqueous solution. For example, at 25° the solubility of $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$, calculated as TiO_2 , in water is 15.3 g./liter, while at a concentration of 300 g./liter of H_2SO_4 and 300 g./liter of $(\text{NH}_4)_2\text{SO}_4$ the solubility drops to 0.8 g./liter. Consequently, the $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ can be salted out from an aqueous solution by the addition of ammonium sulfate and sulfuric acid. Practically complete salting out is achieved when the concentration of the free ammonium sulfate and sulfuric acid in the solution is of the order of 500-600 g./liter.

The $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ crystals do not effloresce in the air, they are not hygroscopic, and they can be kept as long as desired without suffering change in chemical composition.

When heated the salt decomposes according to the reactions:



Titanium dioxide is obtained as a fluffy white powder with an octahedral structure when the pure salt is ignited. If the ignition temperature exceeds 1000° the octahedrite is transformed into rutile.



Fig. 1. Double titanyl ammonium sulfate $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$; 48 x.

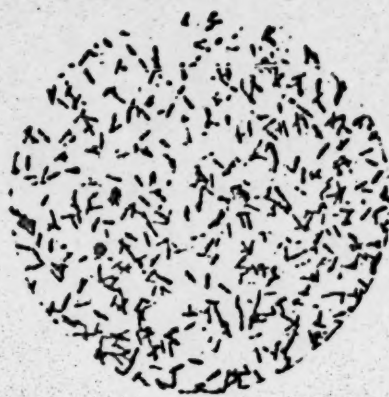


Fig. 2. Double titanyl ammonium sulfate $\alpha\text{-(NH}_4)_2\text{TiO}(\text{SO}_4)_2$; 48 x.



Fig. 3. Double titanium ammonium sulfate $(\text{NH}_4)_2\text{Ti}(\text{SO}_4)_2$; 55 x.



Fig. 4. Double sulfate $2(\text{NH}_4)_2\text{SO}_4 \cdot 3\text{TiOSO}_4 \cdot \text{Ti}(\text{SO}_4)_2$; 50 x.

A study of the ionic conductivity in aqueous solution revealed that the concentration of titanium in the anode area shows increase in measure with current passage. It follows that the double titanyl ammonium sulfate should be regarded as being a complex with the composition $(\text{NH}_4)_2[\text{TiO}(\text{SO}_4)_2]$. However, in aqueous solution the complex ion shows a high degree of dissociation, as a result of which the indicated compound belongs to the class of double salts.

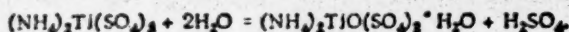
The anhydrous salt $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2$ was obtained in two crystalline modifications. The modification designated as α is salted out when an aqueous titanyl sulfate solution is treated with ammonium sulfate and sulfuric acid at a temperature not exceeding 40° . This modification can also be obtained at room temperature from solutions rich in ammonium sulfate and sulfuric acid. The pure $\alpha\text{-(NH}_4)_2\text{TiO}(\text{SO}_4)_2$ is obtained in the same manner as the pure monohydrate. It is a white powder, nonhygroscopic, and stable in the air. It crystallizes as fine elongated plates or as needlelike crystals (Fig. 2), anisotropic with straight extinction, $N_g = 1.707 \pm 0.005$, $N_p = 1.600 \pm 0.010$.

The second modification, designated as β , was obtained by the dehydration of $(\text{NH}_4)_2\text{TiO}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ in an oven at a temperature of about 200° . The crystals of the β -modification are idiomorphic with the crystals of the monohydrate; however, they show slight double light refraction. The refractive index of the $\beta\text{-(NH}_4)_2\text{TiO}(\text{SO}_4)_2$

crystals is around 1.629; β -(NH_4) $_2$ TiO(SO $_4$) $_2$ is unstable in the air, and drawing moisture, is transformed into (NH_4) $_2$ TiO(SO $_4$) $_2$ ·H $_2$ O.

The double sulfates, (NH_4) $_2$ Ti(SO $_4$) $_3$ and 2(NH_4) $_2$ SO $_4$ ·3TiOSO $_4$ ·Ti(SO $_4$) $_2$, were obtained from the melts of titanium dioxide with ammonium sulfate and sulfuric acid.

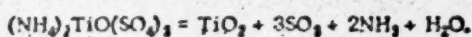
The salt (NH_4) $_2$ Ti(SO $_4$) $_3$ crystallizes from the melt as coarse, platelike monoclinic crystals (Fig. 3) at a temperature above 230°. The crystals of the salt are white with a greasy lustre, anisotropic, and with a straight angle of extinction, $N_g = 1.754 \pm 0.010$, $N_p = 1.684 \pm 0.010$. The salt is insoluble in water, but slowly decomposes according to the reaction.



Due to its instability in the presence of moisture the (NH_4) $_2$ Ti(SO $_4$) $_3$ crystallizes only from melts that contain a small amount of water and boil above 200°. The H $_2$ SO $_4$:(NH_4) $_2$ SO $_4$ ratio in the melt should be around 2, but it can show change within fairly wide limits, both in the direction of increase and especially in the direction of decrease.

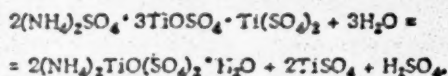
The (NH_4) $_2$ TiO(SO $_4$) $_2$ crystals are decomposed slowly by cold water. Below 20° in the presence of water the salt is converted completely to the corresponding titanyl sulfate salt in only a day. This fact can be used to obtain the pure salt in the following manner. The melt containing the crystals of this salt, is treated with a large excess of water at a temperature below 20°. The filtered crystals are first washed with cold water, then with 96% alcohol, and dried at 100-110°. The dried crystals can be kept indefinitely only in a tightly stoppered vessel.

When heated at 450-500° the (NH_4) $_2$ TiO(SO $_4$) $_2$ decomposes according to the reaction



The presence of the double salt 2(NH_4) $_2$ SO $_4$ ·3TiOSO $_4$ ·Ti(SO $_4$) $_2$ was shown in the melts of titanium dioxide with ammonium sulfate and sulfuric acid that boil around 200°. When the melts have a higher boiling point, i.e., when the water content of the melts is lower (the boiling point of the melt is primarily determined by the water concentration), the crystals of this salt go into solution and (NH_4) $_2$ Ti(SO $_4$) $_3$ is obtained as a precipitate.

The pure 2(NH_4) $_2$ SO $_4$ ·3TiOSO $_4$ ·Ti(SO $_4$) $_2$ is obtained in the same manner as was the above described (NH_4) $_2$ Ti(SO $_4$) $_3$. The crystals of this salt are white, anisotropic, $N_g = 1.755 \pm 0.010$, $N_p = 1.670 \pm 0.005$. The salt crystallizes as tiny rhombic prisms (Fig. 4). It is unstable in water and slowly decomposes as indicated by the reaction



The examined salt is of interest for the reason that both the normal and basic titanium sulfates enter into its composition. It appears as a transition compound between the two types of double titanium salts: those based on titanyl sulfate and those based on normal titanium sulfate.

The instability of the double salts based on normal titanium sulfate to water is indirect proof that it is impossible for normal titanium sulfate, Ti(SO $_4$) $_2$, to exist in aqueous solutions. This compound can probably exist only in anhydrous media and under the influence of water is converted into the basic sulfate or is hydrolyzed to titanium hydroxide.

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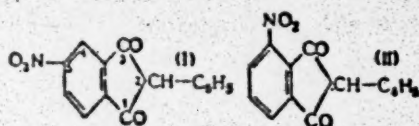
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4-NITRO-2-PHENYL-1,3-INDANDIONE

V. N. Zelmen and G. Ya. Vanag

(Presented by Academician B. A. Kazansky, February 22, 1956)

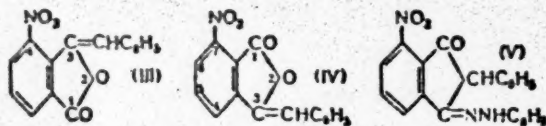
2-Phenyl-1,3-indandione finds use as a blood anticoagulant and as a rodenticide. For the purpose of increasing its toxicity in the latter case it seemed of interest to synthesize those nitro derivatives of phenylindandione in which the nitro group is found in the phthalyl ring. Of these the 5-nitro-2-phenyl-1,3-indandione (I) is described in the literature, while attempts to prepare the 4-nitro-2-phenyl-1,3-indandione (II) have failed up to now. However, in order to study the influence of the nitro group on the physiological activity of compounds as a function of the nitro group position it was important to prepare compound (II).



2-Phenyl-1,3-indandione and many of its derivatives are frequently prepared by the isomerization of the corresponding benzalphthalides with sodium methylate in methanol solution, while the benzalphthalides are obtained either by condensation of the corresponding phthalic anhydride with phenylacetic acid in the presence of anhydrous sodium acetate or by condensation of the corresponding phthalide with benzaldehyde.

Leupold [1] condensed the anhydrides of nitrophthalic acids with phenylacetic acid for the purpose of obtaining the corresponding benzalphthalides, but here he was successful in obtaining condensation only with 4-nitrophthalic anhydride. Pronounced tarring occurred when he used the 3-nitrophthalic anhydride and he was unable to isolate any reaction products. Recently these experiments were repeated by Escola [2] and Klosa [3] and isomerization of the obtained nitrobenzalphthalides gave them 5-nitro-2-phenyl-1,3-indandione (I).

We were successful in finding conditions under which the 3-nitrophthalic anhydride condenses with phenylacetic acid to give the corresponding nitrobenzalphthalide, and isolated the latter in 22% yield. Here the formation of the two nitrobenzalphthalides (III) and (IV) is theoretically possible. Judging from the properties of the isolated substance, here we obtained an individual compound, and not a mixture of the two isomers, as is the case for the 4-nitrophthalic anhydride. Of the two possible isomers - 4-nitro-3-benzalphthalide (III) and 7-nitro-3-benzalphthalide (IV) - we feel that the latter (IV) is the more probable.



Isomerization of the obtained nitrobenzalphthalide with sodium methylate in methanol solution gave us the desired 4-nitro-2-phenyl-1,3-indandione (II) as red crystals. It was characterized by preparing its phenylhydrazone, semicarbazone and anil, in which connection the mono-derivative, probably of the (V) type, is always formed.

EXPERIMENTAL

4-Nitrobenzalphthalide (III). A mixture of 27 g of phenylacetic acid (m.p. 75°), 35.5 g of 3-nitrophthalic anhydride (m.p. 163-164°) and 1 g of anhydrous sodium acetate was thoroughly stirred until homogeneous. The mixture was placed in a short-necked flask, fitted with a thermometer and wide outlet tube, and heated rapidly in a sand bath to 200° (thermometer in the mixture). Reaction set in and water began to drip from the outlet tube. Then the mixture was heated cautiously, making sure that the temperature did not rise above 225-230°. Vigorous decomposition began above this temperature: the phenylacetic acid distilled and the residue in the flask turned into a black tarry mass, from which the 4-nitrobenzalphthalide could no longer be isolated.

About 2-3 ml of water distilled if the indicated temperature regime was observed, after which the temperature dropped rapidly. Heating was discontinued, the mixture was permitted to cool slightly, and the viscous brown liquid was poured into alcohol (approximately 150 ml). Yellow needles of 4-nitrobenzalphthalide deposited. To remove any unreacted 3-nitrophthalic anhydride and phenylacetic acid the precipitate was boiled with water and the hot solution filtered. There remained 11 g of 4-nitrobenzalphthalide (22.4% of theory) on the filter. After recrystallization from glacial acetic acid or alcohol, m.p. 153-154°.

Found %: N 5.42. $C_{15}H_9O_4N$. Calculated %: N 5.24.

4-Nitro-2-phenyl-1,3-indandione (II). A mixture of 5 g of 4-nitrobenzalphthalide, 25 ml of methanol and 50 ml of 3% sodium methylate (prepared by dissolving 1.5 g of sodium in methanol) was heated on the water bath until the nitrobenzalphthalide had dissolved completely. The dark red solution was filtered. A small amount of yellow amorphous substance remained on the filter. The filtrate was diluted with water and acidified with concentrated hydrochloric acid. Here a red precipitate was obtained, appearing under the microscope as slender feltlike interlaced needles. The yield of 4-nitro-2-phenyl-1,3-indandione was 4.7 g (94% of theory). The substance can be recrystallized from alcohol, glacial acetic acid and other organic solvents. M.p. 131-133° with decomposition.

Found %: N 5.35. $C_{15}H_9O_4N$. Calculated %: N 5.24.

Phenylhydrazone (V). A solution of 4-nitro-2-phenyl-1,3-indandione in glacial acetic acid was heated with excess phenylhydrazine. Tiny brown needles. M.p. 183-184° with decomposition.

Found %: N 11.93. $C_{21}H_{15}O_3N$. Calculated %: N 11.77.

Semicarbazone. A water solution of 0.6 g of semicarbazide hydrochloride and 0.44 g of sodium bicarbonate was added to an alcohol solution of 0.5 g of the 4-nitro-2-phenylindandione and the mixture heated on the water bath for 2 hours. Here a finely crystalline pale-yellow precipitate was obtained, m.p. 222-225°, with decomposition; after recrystallization from glacial acetic acid, m.p. 229-230° with decomposition.

Found %: N 17.48. $C_{16}H_{12}O_4N_4$. Calculated %: N 17.30.

Anil. A solution of 4-nitro-2-phenyl-1,3-indandione in glacial acetic acid was heated with excess aniline for 2 hours. The red crystalline anil precipitated. After recrystallization from glacial acetic acid, m.p. 240-241° with decomposition.

Found %: N 8.21. $C_{21}H_{14}O_3N_2$. Calculated %: N 8.19.

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Received January 9, 1956;

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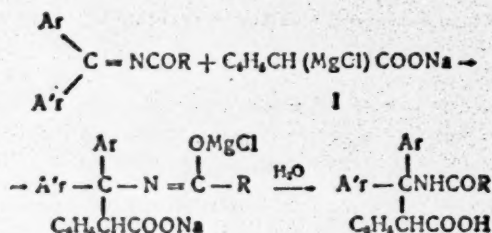
SYNTHESIS OF α -PHENYL- β , β -DIARYL- β -(N-BENZOYL)-AMINOPROPIONIC ACIDS FROM N-BENZOYLBENZOHYDRYLIDENIMINES AND SODIUM α -CHLORO-MAGNESIUMPHENYLACETATE

Khr. Ivanov

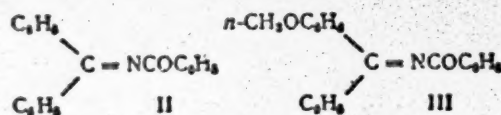
(Presented by Academician I. N. Nazarov, May 5, 1956)

It has been shown recently that the reaction of sodium α -chloromagnesiumphenylacetate (I) with anils yields β -anilino acids, and with hydramides it yields β -amino acids [2,3].

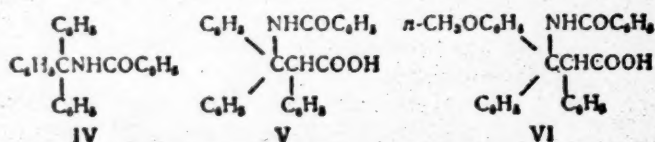
In this connection it seemed of interest to study the possibility of adding I to N-acylated aromatic ketimines. It was hoped that the reaction would proceed by the scheme:



as a result of which the unknown N-acyl derivatives of α -phenyl- β , β -diaryl- β -aminopropionic acids would be obtained. In this paper we describe the reaction of (I) with N-benzoylbenzohydrilidenimine (II) and with N-benzoyl-p-methoxybenzohydrilidenimine (III).

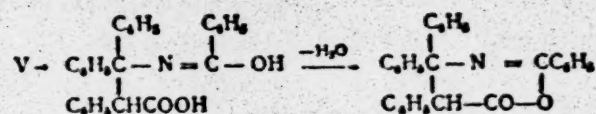


Since the literature is devoid of any information on the behavior of acylketimines toward organomagnesium compounds, we first studied the reaction of II with phenylmagnesium bromide. Here it was found that the latter adds smoothly to the system of conjugated double bonds present in this acylketimine to give the compound N-benzoyltriphenylmethylaniline (IV).



The experiments made on the addition of I to II and III revealed that the desired reaction takes place in both cases. Here α,β,β -triphenyl- β -(N-benzoyl)-aminopropionic acid (V) and α,β -diphenyl- β -(p-methoxyphenyl)- β -(N-benzoyl)-aminopropionic acid (VI) were respectively obtained in good yields. Due to the low solubility of N-benzoyldiaryl ketimines in ether the syntheses were run in ether-benzene medium. Attempts to increase the yields by using higher boiling solvents (dioxane, ether-toluene mixture) proved unsuccessful.

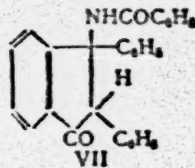
Acid V was boiled with acetic anhydride for the purpose of proving the β -position of the benzoylamino group in the synthesized acids. It was postulated that under these conditions the benzoylamino acid, similar to other β -amino acids, would be desaminated. However, instead of the expected α,β -diphenylcinnamic acid, we obtained a neutral nitrogen-containing substance with m.p. 204-205°, which from the nitrogen content corresponds to the dehydration product of acid V. The stability of the given substance to alkali shows that it does not contain the methoxazine ring, which would be formed by closure if the dehydration proceeded by the scheme:



D. Ivanov and Ch. Ivanov [4,5] established that α,β,β -triphenyl- β -hydroxypropionic acid under the influence of conc. sulfuric acid is transformed through 3-hydroxy-2,3-diphenyl-1-hydrindone into 2,3-diphenylindone; under longer exposure to sulfuric acid the latter is sulfonated.

In view of the analogy in the structure of the studied β -benzoylamino acids and α,β,β -triphenyl- β -hydroxypropionic acid it could be expected that they would show analogous behavior in conc. sulfuric acid. And in fact, under prolonged treatment with sulfuric acid, acid V is transformed into 2-[p-sulfophenyl]-3-phenylindone (identified as the sodium salt). However, under short treatment with sulfuric acid the main reaction product is again the substance with m.p. 204-205°. We were unable to establish the formation of 2,3-diphenylindone, evidently for the reason that together with desamination of the intermediate product, which should be the substance with m.p. 204-205°, the latter also suffers simultaneous sulfonation.

Although, as far as we know, the transition of β -amino acids into indone derivatives has been achieved for the first time here, we believe that the facts found by us support the β -position of the benzoylamino group in the initial benzoylamino acid and give basis to the assertion that the compound with m.p. 204-205° is 3-benzoylamino-2,3-diphenyl-1-hydrindone (VII).



EXPERIMENTAL

The starting N-benzoyldiaryl ketimines were obtained by the method of Moureu and Mignonac [6].

N-Benzoylbenzohydrylideneimine (II). This compound is known [7,8]. We synthesized it as follows. The boiling for 3 hours of 7.73 g (0.075 mole) of benzonitrile with excess phenylmagnesium bromide gave $(\text{C}_6\text{H}_5)_2\text{NMgBr}$, the ether layer was decanted from the reaction crystals, and the latter were washed with absolute ether and then suspended in 35 ml of the same solvent. A solution of 16.86 g of benzoyl chloride in an equal volume of ether was added to the suspension. The mixture was boiled for 3 hours, cooled, and the ether layer decanted. The residue was washed twice with absolute ether and then decomposed with absolute alcohol under heating. The alcohol solution was filtered and after several hours 15.10 g (70%) of N-benzoylbenzohydrylideneimine deposited from the filtrate, and recrystallized from ethyl acetate. M.p. 116-118° (from [7,8], m.p. 117-118°).

Found %: N 4.80, 4.84.

$C_{25}H_{11}NO$. Calculated %: N 4.91.

N-Benzoyl-p-methoxybenzohydrazide (III). To a suspension of $p\text{-CH}_3\text{OCH}_2\text{H}_2\text{C}(\text{=NMgBr})\text{C}_6\text{H}_5$, obtained from 4.60 g (0.045 mole) of benzonitrile and an excess of p-anisylmagnesium bromide, in 30 ml of absolute ether was added 8.40 g of benzoyl chloride (in an equal volume of absolute ether) and the mixture was boiled for 4 hours. The precipitate was washed with absolute ether and decomposed with absolute alcohol. The alcohol solution was filtered, cooled, poured into 150 ml of water, and acidified with acetic acid. The resulting oil was washed with water and rubbed with a glass rod, when slow crystallization set in. The crystals were rubbed with a small amount of alcohol, filtered, and recrystallized from ethyl acetate. Yield 6.80 g (48%). M.p. 105-108°. After a second recrystallization the product melts at 106-108°.

Found %: N 4.25, 4.28.

$C_{21}H_{17}NO_2$. Calculated %: N 4.44.

N-Benzoyltriphenylmethylamine (IV). To an ether solution of phenylmagnesium bromide, obtained from 0.40 g of magnesium and 2.40 g of bromobenzene, was added 3.30 g (0.015 mole) of II, dissolved in 30 ml of absolute benzene. The mixture was boiled for 1 hour. The next day the usual treatment gave 2.60 g (about 62% of N-benzoyltriphenylmethylamine, which was recrystallized from alcohol. M.p. 164-165° (from [9], m.p. 165.5°).

Found %: N 3.89, 3.84.

$C_{24}H_{21}NO$. Calculated %: N 3.85.

The boiling of 0.50 g of IV with conc. hydrochloric acid for 8 hours gave 0.10 g of benzoic acid and 0.22 g of a crystalline substance. After three recrystallizations from alcohol the latter melts at 159-161°, the same as its mixture with triphenylcarbinol.

α,β,β -Triphenyl- β -[N-benzoyl]-aminopropionic Acid (V). The necessary $C_6H_5CH(MgCl)COONa$ was obtained by the method of [10] from 0.24 g of magnesium, 1.00 g of isopropyl chloride and 1.58 g (0.01 mole) of sodium phenylacetate. To its suspension in 45 ml of ether was added 2.14 g (0.0075 mole) of II, dissolved in 15 ml of absolute benzene. A precipitate formed. After 6-hour boiling on the water bath the mixture was decomposed with ice water and hydrochloric acid. The crystals were removed and the ether-benzene solution was extracted with 5% alkali. The alkaline extract and crystals were combined and heated until the latter dissolved. The solution was filtered and poured into 100 ml of 1:1 hydrochloric acid. The precipitate was filtered, washed with water, and boiled for 10 minutes with 5-6 ml of alcohol. After cooling there was isolated 1.55 g (49%) of crystals with m.p. 234-235°, which were recrystallized from ethyl acetate. M.p. 238-239° (with decomposition).

Found %: N 3.30, 3.34.

$C_{27}H_{23}NO_3$. Calculated %: N 3.32.

α,β -Diphenyl- β -[p-methoxyphenyl]- β -[N-benzoyl]-aminopropionic Acid (VI). This compound was synthesized in the same manner as acid V. The yield was 53% of the theoretical. The crude acid melts at 210-212°, and after recrystallization from either alcohol or ethyl acetate, it melts at 214-215° (with decomposition).

Found %: N 3.06, 3.08.

$C_{29}H_{25}NO_4$. Calculated %: N 3.10.

Action of Acetic Anhydride on Acid V. A mixture of 1 g of V and 5 ml of acetic anhydride was boiled for 5 hours. Hydrolysis with water and neutralization with alkali gave 0.90 g of crystals, which were recrystallized from ethyl acetate. M.p. 204-205°. With conc. sulfuric acid the product gives a dark green color. It does not undergo change when treated with 10% sodium hydroxide for 2 days.

Found %: N 3.43, 3.47.

$C_{28}H_{21}NO_3$. Calculated %: N 3.47.

Action of Conc. Sulfuric Acid on Acid V. a) Acid V (0.50 g) was shaken with 5 ml of sulfuric acid

(d 1.84). The resulting dark green solution was allowed to stand for 5 hours. Further treatment was by the Ch. Ivanov method [5]. We isolated 0.18 g (about 40%) of the sodium salt of 2-[p-sulfophenyl]-3-phenylindone (identified by its mixed melting point with an authentic specimen), 0.05 g of substance with m.p. 204-205° (identical with the reaction product of acid V with acetic anhydride) and 0.05 g of mixed unchanged starting acid V and benzoic acid.

b) A mixture of 0.50 g of acid V and 5 ml of conc. sulfuric acid was shaken for 5 minutes and worked up the same as in the first case. We isolated 0.25 g substance with m.p. 204-205°.

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THE THERMAL DECOMPOSITION OF LITHIUM ALUMINUM HYDRIDE

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(Presented by Academician L. I. Chernyaev, February 29, 1956)

The reducing properties of lithium aluminum hydride, so strongly manifested in reactions proceeding in ether medium [1], can also appear if the lithium aluminum hydride is heated alone with the substance being reduced. To use lithium aluminum hydride under these conditions it was interesting to determine the point at which its thermal decomposition began and also the rate of hydrogen evolution with increase in temperature.

The lithium aluminum hydride was prepared by a modification of the method used by Schlesinger and co-workers [2]; the white, well formed crystals analyzed 98% $LiAlH_4$; the remainder was its hydrolysis products.

For the thermal decomposition study a 0.1-0.2 g sample of the compound was placed in a small quartz crucible, lined with magnesium oxide, where one junction of a combination thermocouple of the type used for differential thermal analysis [3] was inserted. The second junction of the thermocouple was placed in a similar crucible, filled with fused aluminum oxide, which was taken as the standard.

Both crucibles were placed in a quartz test tube, connected to a gas burette. The test tube was heated in an electric oven fitted with a heat regulator, which permitted obtaining a heating rate of 2-3°.

The thermocouple readings, both direct and differential, were recorded with a pyrometer of the N. S. Kurnakov type. Prior to the start of heating the test tube with substance was thoroughly evacuated and then filled with nitrogen. In subsequent heating a recording of the temperature change and a visual reading of the amount of hydrogen evolved were made at the same time.

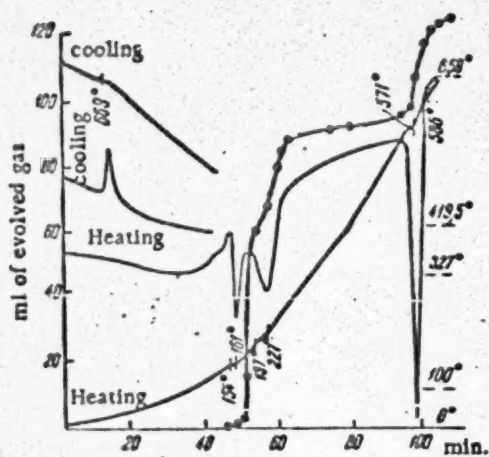


Fig. 1

An example of a thermogram for the heating of 0.113 g of lithium aluminum hydride and the subsequent cooling of its thermal decomposition product is shown in Fig. 1. An examination of the thermogram reveals that lithium aluminum hydride shows complete thermal stability up to 140-145°. Some hydrogen evolution begins above this temperature, accompanied by heat absorption. The heating curve shows three endothermic effects, noted on both the direct and, with especial clarity, on the differential heating curve. This heat effect is due to the intense evolution of hydrogen, which proceeds in several stages. At first approximately half of all of the hydrogen contained in the compound is evolved at 154-161°, then another one fourth is evolved at 197-227°, and finally, the remainder of the hydrogen is evolved at 580-586°, at the same time being accompanied by melting of the specimen. As a whole the hydrogen evolution is quantitative — about 130 ml.

From the cooling curve data, which show an exothermic effect at 689°, the decomposition product is a binary aluminum-lithium alloy, containing 15-16% of lithium [4]. The composition of this alloy is shifted somewhat, with its eutectic point corresponding to fusion of the Al-Li compound at 718°, apparently due to partial reaction of the lithium with the crucible lining material.

The results of the present study are of interest for the reason that they show both the thermal stability of lithium aluminum hydride up to a temperature of 140-150° and the steplike character of hydrogen evolution during its thermal decomposition in the interval 150-586°. On the other hand, the formation of a binary aluminum-lithium alloy in the thermal decomposition of lithium aluminum hydride indicates that in principle we have here a new method of obtaining aluminum alloys. If all of the operations involved in the synthesis of lithium aluminum hydride and in its thermal decomposition are run under conditions that exclude the presence of traces of both moisture and air, we can then obtain the alloys in a high state of purity.

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ALKYLATION OF FERROCENE

Academician A. N. Nesmeyanov and N. S. Kocherikova

The alkylation of ferrocene with alkyl halides in the presence of aluminum chloride has not been described in the literature. It was communicated very recently by Riemschneider and Helm [11] that the Friedel-Crafts reaction has no general significance for ferrocene. They were able to acylate ferrocene using oxalyl chloride, and to alkylate it with ethyl bromide, isopropyl chloride and benzyl chloride in carbon disulfide.

We were the first to accomplish the alkylation of ferrocene with alkyl halides in the presence of anhydrous aluminum chloride. As solvent we used an excess of the alkyl halide.

Thus, from ferrocene and ethyl bromide we obtained the mono-, di- and polysubstituted ethylferrocenes; from n-butyl chloride the mono-, di- and polysubstituted butylferrocenes (with the structure of the butyl group being unknown); from dichloroethane we obtained diferrocenyldichloroethane and higher molecular products, and from benzyl chloride we obtained benzylferrocene. In general the total yield of the alkylation products was of the order of 20-30%.

Some of the above compounds were also recently obtained by one of us with N. A. Volkenau [9] in the Clemmensen reduction of ferrocene ketones. The lower alkylferrocenes are red liquids, capable of being distilled *in vacuo* without decomposition. The polyalkylferrocenes are viscous red oils with b.p. 180-220° at 3-5 mm.

The fact that ferrocene can be alkylated by the Friedel-Crafts method is new evidence of its aromatic nature [1-10].

Ethylation of Ferrocene. To a solution of 40 g of dry ferrocene (m.p. 173°) in 150 ml of ethyl bromide at room temperature and with stirring was added 15 g of anhydrous aluminum chloride (heat was evolved). Then with constant stirring the reaction mixture was heated at the boil for 5 hours, after which it was cautiously decomposed at first with ice, and then with a mixture of ice and 10% hydrochloric acid. To the mixture, which separated into two dark layers that were hard to distinguish, was added 10 g of sodium sulfite; after filtration the lower red-brown layer was separated and dried over calcium chloride. The ethyl bromide was removed by distillation (80 ml, which was re-usable in the synthesis after ordinary purification); the residue was vacuum-heated for a long time (115° at 25 mm); here 1.5 g of ferrocene was recovered by sublimation. The oily residue was then fractionally distilled *in vacuo*. The yield of monoethylferrocene was 1.8 g (4% of the theoretical), b.p. 107-108°/5 mm, n_D^{20} 1.6011, d_4^{20} 1.2470.

Found %: C 67.84, 67.82; H 6.70, 6.88; Fe 25.50, 25.56.

$C_{12}H_{14}Fe$. Calculated %: C 67.32; H 6.55; Fe 26.13.

The dark red oil, insoluble in water, is readily soluble in organic solvents.

We also obtained 1.9 g (3.5% of the theoretical) of diethylferrocene, b.p. 120-123°/5 mm, n_D^{20} 1.5852,

Found %: C 69.73, 69.58; H 7.32, 7.23; Fe 23.00, 22.82.

$C_{14}H_{18}Fe$. Calculated %: C 69.51; H 7.40; Fe 23.09.

This compound is also a dark red oil, insoluble in water, and readily soluble in organic solvents.

We also obtained 2.0 g (3.5% of theory) of mixed triethylferrocene isomers, b.p. 145-153°/5 mm.

Found %: C 70.76, 70.59; H 7.53, 7.59; Fe 21.10, 21.41.
 $C_{18}H_{12}Fe$. Calculated %: C 71.20; H 8.15; Fe 20.65.

Butylation of Ferrocene. Under similar conditions (heating for 8 hours at 70-75°) from 40 g dry ferrocene, 170 ml of n-butyl chloride and 15 g of anhydrous aluminum chloride we obtained 3.1 g (7.6% of theory) of monobutylferrocene, b.p. 108°/3.5 mm, n_D^{20} 1.5701, d_4^{20} 1.1859.

Found %: C 70.69, 70.74; H 7.82, 7.69; Fe 21.76, 21.26.
 $C_{14}H_{18}Fe$. Calculated %: C 69.51; H 7.40; Fe 23.02.

Dark red oil, insoluble in water, and readily soluble in organic solvents.

Also 2.5 g (5.2% of theory) of dibutylferrocene, b.p. 155-157°/3.5 mm, n_D^{20} 1.5649, d_4^{20} 1.1432.

Found %: C 73.52, 73.33; H 8.46, 8.69; Fe 17.88, 18.01.
 $C_{18}H_{22}Fe$. Calculated %: C 72.56; H 8.71; Fe 18.73.

Dark red oil, insoluble in water, and readily soluble in organic solvents.

Also 11.5 g (16.5% of theory) of mixed pentabutylferrocene isomers, b.p. 138-150°/7·10⁻⁴ mm. (Analysis of the products, boiling in narrower temperature limits: 138-139°/7·10⁻⁴ mm, 145-146°/7·10⁻⁴ mm, 149-150°/7·10⁻⁴ mm, gave similar results).

Found %: C 77.17, 77.24; H 9.57, 9.70; Fe 12.55, 12.60.
 $C_{20}H_{26}Fe$. Calculated %: C 77.40; H 10.60; Fe 12.00.

Dark red viscous oil with b.p. -19°. Here 7.5 g of ferrocene (m.p. 172°) was recovered.

Benzylferrocene. Under similar conditions from 20 g of ferrocene, 85 ml of benzyl chloride and 6 g of aluminum chloride we obtained 3.5 g of a dark deliquescent mass and recovered 15 g of ferrocene by vacuum distillation. After recrystallization from absolute alcohol and long cooling we obtained 1.5 g of benzylferrocene, m.p. 55-57°.

Found %: C 74.33, 74.19; H 6.10, 6.21; Fe 19.28.
 $C_{17}H_{14}Fe$. Calculated %: C 73.97; H 5.81; Fe 20.22.

Benzylferrocene is a yellow crystalline substance, readily soluble in ether, benzene, dioxane and petroleum ether, less readily soluble in aqueous alcohol, and insoluble in water.

Diferrocenyloethane. Under similar conditions we reacted 20 g of well-dried ferrocene (m.p. 173°), 75 ml of dry dichloroethane and 6 g of anhydrous aluminum chloride. After decomposing the reaction mass in the usual manner the product was isolated as follows. After removing the solvent and heating with superheated steam (110-115°) we recovered 7 g of ferrocene. The residual tarry mass dissolved almost completely in 100 ml of 1:1 nitric acid (dark green solution); the addition of excess sodium sulfite gave an egg-yellow microcrystalline precipitate of diferrocenyloethane, which after recrystallization from absolute alcohol melted in a sealed capillary at about 135°. The yield was 11.5 g (27% of theory).

Found %: C 66.66, 66.71; H 5.66, 5.63; Fe 27.60, 27.61.
 $C_{22}H_{12}Fe_2$. Calculated %: C 66.49; H 5.54; Fe 27.97.

Diferrocenyloethane is a yellow crystalline substance, readily soluble in ether, benzene, dioxane and petroleum ether, less readily soluble in aqueous alcohol, and insoluble in water.

When the amount of aluminum chloride was increased to 10 g and the reaction time to 25 hours we obtained, together with other products, 1 g of a brown powdery high-molecular polymer. When the polymer was oxidized with 0.1 N potassium dichromate in sulfuric acid solution under static conditions it proved to have an oxidation capacity of 2.8-3.5 mg.-equiv. per gram of air-dried resin. The reduction was run with excess ascorbic acid. This high polymer is the first known member of the organolron electron-exchange resins.

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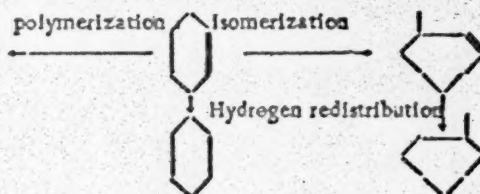
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CONVERSION OF CYCLOHEXENE ON DEUTERATED ALUMINOSILICATE CATALYST

G. M. Panchenkov, Z. V. Gryaznova and L. G. Ganichenko

(Presented by Academician B. A. Kazansky, January 3, 1956)

The conversion of cyclohexene on aluminosilicate catalysts has been repeatedly used to study the properties of these catalysts. A. A. Petrov and V. V. Shchekin [1], in studying the conversion of cyclohexene on synthetic aluminosilicate at 260-316°, showed that the monomer fraction contains cyclohexane, cyclohexene, methylcyclopentane and methylenecyclopentane, while the polymer fraction (composed mostly of the dimer) contains cyclohexylmethylcyclopentane and phenylmethylcyclopentane, i.e., the same products that were found by N. D. Zelinsky and co-workers in the isomerization of cyclohexene on oxides [2-4]. It was shown by K. V. Tepchleva [5] that cyclohexene at 350° in the presence of an aluminosilicate catalyst undergoes the following transformations:



In the above cited work it was found that the isomerizing action of the catalyst increases as its aluminum oxide content is increased up to 16%. Further increase in the aluminum oxide content of the catalyst does not affect its isomerization activity.

In our work we used a deuterated aluminosilicate catalyst composed of 35.5% Al_2O_3 and 64.5% SiO_2 , and containing 185m-equiv of D per 100 g of catalyst [6]. The reaction temperature was 350°, and the space velocity was varied in the limits of 0.13 to 3.00 $\frac{\text{volume of substance}}{\text{volume of catalyst} \cdot \text{hour}}$. Automatic feeding of the cyclohexene to the catalyst was used. The experiments were run in a flow system. The apparatus was similar to that used to study the cracking of cumene [6]. The cyclohexene was obtained by passing cyclohexanol over anhydrous magnesium sulfate at 300° in a slow stream of dry nitrogen. The catalyzate was dried for a day over fused calcium chloride, and then it was boiled for 40 minutes with metallic sodium in a Favorsky flask, after which it was distilled. The constants of cyclohexene obtained in this manner were: b.p. 83°/760 mm; n_D^{20} 1.4469; d_4^{20} 0.8095.

The catalyzate from the cyclohexene isomerization was collected in a receiver, cooled in a mixture of dry ice and methyl alcohol, and then distilled from a quartz Favorsky flask into the monomer (up to 85°) and polymer (above 85°) fractions. To determine the percent conversion by isomerization a part of the monomer fraction was hydrogenated over nickel-on-aluminum oxide catalyst (containing 30 mole % nickel) at 180° and a space velocity of 0.15. This catalyst had long constant activity.

The hydrogenation was run until a constant refractive index was obtained. The refractive index of the hydrogenation products was measured on an IRF-22 refractometer with an accuracy of ± 0.0002 . As experiment

revealed, the hydrogenation was complete in one pass of the substance over the catalyst. From Table 1 it can be seen that a second hydrogenation of this fraction did not change its index of refraction.

Hydrogenation of the monomer fraction gave a mixture of cyclohexane and methylcyclopentane. The amount of methylcyclopentane in the hydrogenated portion of the catalyzate corresponds to the sum of the methylcyclopentene and methylcyclopentane, and shows the percent of isomers in the monomer fraction. The amount in percent of both components (methylcyclopentane and cyclohexane) was determined from the graph showing the relationship between refractive index and composition [7].

The presence of deuterated products does not influence the refractive index of the mixture, since the refractive index of wholly deuterated methylcyclopentane differs from the refractive index of the nondeuterated compound by a value that is within the limits of error of our measurements [8]; in our case partially deuterated products were present.

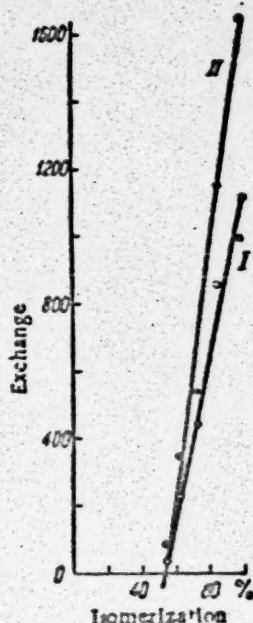


Fig. 1. Relationship between the amount of heavy hydrogen in the monomer (I) and polymer (II) fractions and the degree of isomerization.

percent conversion based on isomerization is still very large (50%). With space velocities above 3 for the cyclohexene the isomerization process is still quite profound, but the exchange of hydrogen by the hydrocarbons for the deuterium of aluminosilicate catalysts is practically nonexistent (see Table 1). In the case of the examined reaction the exchange of the two kinds of hydrogen ceases completely when the space velocity is increased 22 times, while in the case of cumene cracking on a deuterated aluminosilicate catalyst, as we had shown [6], the exchange of the two kinds of hydrogen ceases when the cumene feed rate is only doubled. In both cases the amount of hydrogen exchanged between the catalyst and the hydrocarbons slows more rapidly with space velocity increase than does the amount of transformed hydrocarbons in the final products of isomerization and polymerization or cracking, and the amount of deuterium migrating to the hydrocarbons shows regular diminution in proportion to the amount contained in the catalyst.

From our experimental data on the relationship between the percent of cyclohexene isomerization and the space velocity (Table 1) it is possible to derive a kinetics equation that characterizes this process. It was shown by calculation that the isomerization reaction obeys the equation

$$k = n_0 \frac{B}{bl} [-\ln(1-x) - x]$$

The residues from the monomer and polymer fractions were burned in a quartz apparatus in a stream of pure dry air over copper oxide at 700°. The water that was obtained was purified by the method used to purify small quantities [9] and was analyzed for the amount of heavy hydrogen by the method of finding the temperature at which a quartz float shows flotation equilibrium [10]. The analysis accuracy was $\pm 5\%$. The results are given in Table 1.

From Table 1 it can be seen that when the space velocity increases from 13 to 3.00 $\frac{\text{vol. of substance}}{\text{vol. of catalyst} \cdot \text{hour}}$

the degree of cyclohexene isomerization changes from 100 to 54%. At the same time the degree of deuteration based on reaction of the hydrocarbons with the deuterated catalyst is very greatly diminished. As can be seen from this table, the amount of heavy hydrogen in the monomer and polymer fractions shows a respective decrease of 30- and 20-fold. If we construct a graph showing the relationship between the amount of heavy hydrogen exchanged and the degree of isomerization in percent, we obtain two straight lines that intersect the horizontal axis at about 50% (Fig. 1). As a result, we see that the exchange of hydrogen by the hydrocarbons for heavy hydrogen is completely terminated at a point where the per-

TABLE 1
Experimental Results

Space velocity	Time in minutes	n _D of the monomer fraction after hydro- genation		% conversion by isomeriza- tion	Amount of heavy hydrogen γ	
		Hydro- genation I	Hydro- genation II		monomer fraction	polymer fraction
0.13	60	1.4096	1.4096	100	1116	—
0.13	60	1.4100	1.4100	98	990	1650
0.54	60	1.4120	1.4120	85	857	1148
1.04	50	1.4141	1.4142	73	441	542
1.5	50	1.4160	1.4160	62	229	350
3.0	20	1.4175	1.4175	54	34	88

Here $k = k^*S_0$, where k^* is the true reaction rate constant; S_0 is the catalyst area per unit of layer length; n_0 is the number of moles of starting substance that enters the reaction zone per unit of time; $B = \sum \omega_i b_i$ is the sum of the products of the adsorption coefficients and the stoichiometric coefficients for the decomposition products, hindering the process; l is the length of the catalyst layer; κ is the amount of reacted substance in relative units. The derivation of this equation and its application to different types of reactions on aluminosilicate catalysts are given in the studies of one of us [11-15]. For the examined reaction the apparent rate constant $K = kb/B$ proved to be equal to 0.04.

Both isomerization and exchange took place when cyclohexene was passed over deuterated aluminum oxide, containing 145 m-equiv. D per 100 g of Al_2O_3 , at a space velocity of 0.74 and a temperature of 350°. When the obtained monomer fraction was burned the amount of heavy hydrogen in the water proved to be equal to 515 γ .

Neither cyclohexene isomerization nor exchange of hydrogen by cyclohexene for the deuterium of the catalyst occurred on a deuterated silicon dioxide at 450°.

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EQUILIBRIUM MIXTURES OF FIVE- AND SIX-MEMBERED CYCLENES

A. I. A. Petrov

(Presented by Academician A. V. Topchlev, March 7, 1956)

The problem of the equilibrium concentrations shown by cyclenes at 250-400° was studied in the present work. As catalyst we used aluminum oxide activated by hydrochloric acid, and synthetic aluminosilicate. Equilibrium was approached both from the side of the six-membered cyclenes and the five-membered rings. Our experimental data are given in Table 1, where the concentrations (in volume %) of the hexamethylene hydrocarbons in our obtained catalyzates are indicated.

TABLE 1
Concentration (in Volume %) of Hexamethylene Hydrocarbons in the Obtained Catalyzates

Starting hydrocarbon	On aluminosilicate catalyst			On activated aluminum oxide	
	250°	300°	400°	300°	400°
Cyclohexene	<5	—	—	<5	—
1-Methyl-1-cyclopentene	<5	—	—	<5	—
1-Methyl-1-cyclohexene	61	39	21	18	13
1-Ethyl-1-cyclopentene	55	34	27	20	—
1,2-Dimethyl-1-cyclopentene	20	—	—	—	—
1,3-Dimethyl-1-cyclopentene	15	—	—	—	—
1-Ethyl-1-cyclohexene	65°	39	38°	20	—
1,3-Dimethyl-1-cyclohexene	64	—	—	21	—
1-Propyl-1-cyclohexene	72°	—	—	24	—
Allylcyclohexane	64°	—	—	—	—
1-Butyl-1-cyclopentene	55°	—	—	—	—
1-Hexyl-1-cyclohexene	—	—	—	25	—
1-Heptyl-1-cyclopentene	—	—	—	20	—

* Data taken from the studies [1,2].

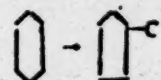
It is evident from these data that the compositions of the isomeric transformation products of cyclenes on aluminosilicate catalyst and on activated aluminum oxide are quite different. Since the isomerization proceeds quite smoothly on an activated aluminum oxide, it follows that the composition of the final isomeric transformation products (with respect to the amount of penta- and hexamethylene hydrocarbons) is approximately the same with any starting cyclene. All of this indicates that practically complete equilibrium is attained. The general tendency shown by six-membered naphenes to become less stable with temperature rise, well known for cyclanes, is also retained for the cyclenes. (Unfortunately, we were unable to obtain any data on the isomerization of cyclenes at 250°, since at this temperature the activated aluminum oxide was characterized by slight activity).

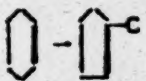
The very deep isomerization shown by cyclohexene into methylcyclopentenes (primarily 1-methyl-1-cyclopentene) attracts attention; this is associated with a large free energy change for the transition of the double bond at the secondary carbon atoms of cyclohexene into a double bond at the tertiary carbon of 1-methyl-1-cyclopentene. In the case of cyclanes, where this situation does not exist, the equilibrium concentrations of methylcyclopentane, both the calculated and those found experimentally, are somewhat smaller (of the order of 75-85%) [3].

Since the free energy values for the cyclenes (other than cyclopentane and cyclohexene) were not determined by us, the changes in the free energy

values in going from a double bond at two secondary carbons to a double bond at a tertiary carbon in cyclenes can only be illustrated by an approximate comparison with the corresponding aliphatic hydrocarbons.

Thus, ΔZ° for the reaction: $\text{C} - \text{C} = \text{C} - \text{C} \rightarrow \text{C} - \text{C} = \text{C} - \text{C}$ equals 1700 cal./mole

(here and later the ΔZ° value is for 600° K, while ΔZ° for the reaction  equals 2080 cal./mole.

From this it is possible to calculate the value for the reaction  as being approximately equal

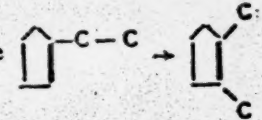
to 3800-4000 cal./mole, which determines the equilibrium concentration of cyclohexene as being in the range of 3-4%.

As first glance, it appears that the data obtained on the aluminosilicate catalyst and on the aluminum oxide are contradictory.

However, it must be remembered that hydrogen redistribution also proceeds on the aluminosilicate catalyst, leading to the formation of cyclanes. This reaction is so pronounced that at the very end, under certain conditions, the catalyzates primarily contain hydrogenated products. We will mention in passing that the saturated products (cyclanes) are chemically inert at these temperatures, and actually fail to participate in the reactions proceeding on the catalyst. All of these considerations serve as good explanations for the high concentrations of hexamethylenes found in the catalyzates of six-membered cyclenes, but the results obtained with ethylcyclopentene and butylcyclopentene require additional explanations.

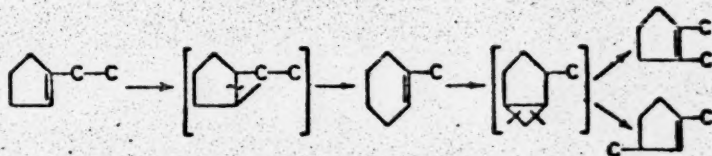
As a matter of fact, the process of hydrogen redistribution among five-membered cyclenes proceeds with no less vigor than for the six-membered cyclenes. It follows that there is no explanation for the fact that large amounts of hexamethylene hydrocarbons are formed in the catalyzates obtained in the transformations of 1-ethylcyclopentene and 1-butyl-1-cyclopentene.

In our opinion, the reason for this phenomenon is to be sought in the relative thermodynamic instability shown by cyclenes with long side chains (for example, the equilibrium concentration of ethylcyclopentane in a mixture of C_7H_{14} cyclanes at 327° is only 15%), and also in the isomerization mechanism prevailing for hydrocarbons of this structural type.

As was mentioned earlier [2], isomerization of the type  apparently proceeds through

series of successive transitions of five-membered cyclenes into six-membered cyclenes and back to the formation of hydrocarbons with the highest thermodynamic stability under the given conditions. Similar opinions relative to the isomerization mechanism of cyclenes and cyclanes have been expressed by other authors [3,4].

The isomerization of 1-ethyl-1-cyclopentene into the stable 1,2- and 1,3-dimethylcyclopentenes can be shown in greater detail by the following scheme:



Here the process goes to completion on the activated aluminum oxide and, in all probability, on the aluminosilicate catalyst there occurs considerable saturation of the intermediate hydrocarbon - methylcyclohexene.

If the starting cyclopentene hydrocarbon has a thermodynamically stable structure, then the ring expansion

reaction proceeds on the aluminosilicate catalyst to approximately the same degree that it does in the presence of the activated aluminum oxide, as can be seen from the examples of 1,2-dimethyl-1-cyclopentene and 1,2-dimethyl-1-cyclopentene isomerization.

The isomerization of the cyclenes was studied in a flow system. The catalyst (aluminum oxide, activated with 1N hydrochloric acid solution [5], or synthetic aluminosilicate) in an amount of 50 ml was charged into a glass reactor, heated in an electric furnace. The crude was added from an automatic burette at a space velocity of 0.6 ml/hour. The collected catalyzate was distilled, and the fraction corresponding to the boiling range of the starting hydrocarbon isomers was collected. Then the fractions obtained from the experiments run on activated aluminum oxide were hydrogenated, the low-boiling on platinized charcoal at 120°, and the high-boiling in an autoclave over Raney nickel.

The amount of hexamethylene hydrocarbons in the hydrogenated products was determined by dehydrogenation over platinized charcoal at 305° and subsequent absorption of the aromatic hydrocarbons in 98% sulfuric acid.

The monomer fractions, isolated from the experiments run on the aluminosilicate catalyst, were again passed through a fresh portion of the aluminosilicate catalyst under the same conditions.

The monomer fractions isolated from the second pass were usually fully saturated (bromine number 2-4). The amount of hexamethylene hydrocarbons in these fractions was then determined as before by dehydrogenation over platinized charcoal.

The hydrocarbons used in our work were obtained by synthesis, and in most cases by the Grignard reaction.

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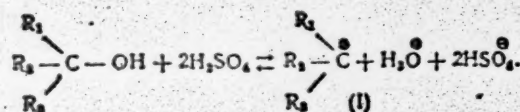
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HYDROGEN EXCHANGE REACTIONS OF 1-METHYL-1-CYCLOHEXANOL WITH PHOSPHORIC ACID

V. N. Setkina and . Corresponding Member, Acad. Sci. USSR D. N. Kussanov

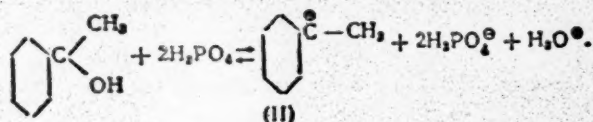
Some new data was recently obtained on the reaction of tertiary alcohols with strong mineral acids. As the result of making some cryoscopic studies of trimethyl- and triethylcarbinol in sulfuric acid solution, Newman, Craig and Garret [1] established that the isotonic coefficient in these cases reaches a value as high as 4. On the basis of this data the reaction of tertiary carbinols with H_2SO_4 was depicted by Equation (1), which postulates the formation of carbonium (D) ions.



Recently V. F. Lavrushin [2] confirmed the formation of carbonium ions of type (D) on the basis of studying the absorption spectra of trimethylcarbinol solutions in concentrated H_2SO_4 .

Consequently, the reaction of tertiary alcohols with strong mineral acids reveals the possibility of obtaining the studying the hydrogen exchange reactions of those carbonium ions that, in contrast to the cases studied by us earlier [3], do not have the hydroxyl group attached to the carbonium carbon.

Using the above as a guide, we studied the hydrogen-exchange reaction of 1-methyl-1-cyclohexanol with deuterium-enriched phosphoric acid. Based on the discussed data the reaction of these substances can be depicted by Equation (2):



The hydrogen exchange experiments with 1-methyl-1-cyclohexanol were run at -5 to 0° . The homogeneous solution, obtained on mixing the alcohol with D_3PO_4 , was poured into aqueous potash solution (the volume of the solution varied from 100 to 700 ml), and the alcohol was extracted with ether and distilled from calcium hydride. The deuterium content in the alcohol was determined by the increase in density of the combustion water, determined by the float method. The results of the experiments on the exchange of hydrogen between 1-methyl-1-cyclohexanol and deuterophosphoric acid are given in Table 1. The reaction was run for 1 hour in Expts. 1-4, for 2 hours in Expts. 5 and 7, and for 4 hours in Expt. 6.

The presence of deuterium in the methylcyclohexyl radical is shown even more clearly in Table 2, where the isotopic analysis data for the 1-methyl-1-cyclohexanol dehydration product, a mixture of methylcyclohexenes, is given.

As a result, it must be considered an experimentally established fact that in the reaction of 1-methyl-1-cyclohexanol with deuteriophosphoric acid the hydrogen atoms of the hydrocarbon radical in this alcohol enter into hydrogen exchange reaction with the acid.

However, this data still cannot be considered as complete evidence that it is specifically the carbonium ion (II) that is involved in the hydrogen exchange reaction. Actually, it is possible to form methylcyclohexenes when 1-methyl-1-cyclohexanol is dissolved in phosphoric acid. It is known the olefins show a greater or lesser tendency to enter into hydrogen exchange reaction with acids. It can also be postulated that the 1-methyl-1-cyclohexanol isolated by us is actually the hydration product of the 1-methyl-1-cyclohexene formed during reaction (by the action of phosphoric acid and water).

Consequently, it would seem possible also to explain the hydrogen exchange shown by 1-methyl-1-cyclohexanol as proceeding through the intermediate formation of the corresponding cycloolefin.

TABLE 1

Expt. No.	Mole ratio alcohol: D_2PO_4	Excess density of alcohol combustion water (in g/ml) calculated *		Exchange in % of the calculated	
		for exchange of all H	for α -H	for all H	for α -H
1	1:0.95	9610	8000	42.0	52.1
2	1:2	17480	13760	88.8	112.8
3	1:2	21000	16820	74.6	97.2
4	1:3	28500	20670	73.8	101.7
5	1:1.3	18360	14380	56.7	72.3
6	1:1.1	16000	13230	32.7	47.1
7**	1:1.1	11000	8750	72.3	91.3

* In calculating the theoretical excess density values of the combustion water it was assumed that the hydrogen of the alcoholic hydroxyl has an isotopic composition corresponding to exchange equilibrium with the hydrogen of the water used to isolate the alcohol.

** Experiment 7 was run with D_2SO_4 in anhydrous ether medium. The ratio alcohol: D_2SO_4 : ether = 1:1.1:1.5.

equimolar amount (based on the cycloolefin) of water, and we also studied the reaction of methylcyclohexene with anhydrous phosphoric acid (see Table 3).

The primary result of all these experiments was to establish the fact that under the conditions used by us to study the hydrogen exchange reaction neither is 1-methyl-1-cyclohexene hydrated nor is 1-methyl-1-cyclohexanol formed. Consequently, the theory that exchange in tertiary alcohols can appear as the result of the immediately formed cycloolefins showing hydrogen exchange does not agree with fact.

This conclusion is also supported by the fact that the 1-methyl-1-cyclohexene recovered from the reaction mixture with deuteriophosphoric acid proved to show a much lower exchange capacity than 1-methyl-1-cyclohexanol under the same conditions.

The above data lead to the conclusion that the hydrogen exchange shown by 1-methyl-1-cyclohexanol in its reaction with phosphoric acid is determined by the equilibrium reaction in which the hydrocarbon carbonium ions participate [Equation (2)].

In the described experiments we were unable to attain exchange equilibrium in the hydrogen exchange reaction of the carbonium ions with phosphoric acid. However, in some of our experiments (for example, Expt. No. 2, Table 1) the number of hydrogen atoms participating in the hydrogen exchange reaction exceeds the number of hydrogen atoms linked to the carbons adjacent to the carbonium center. This data adds support to our theory [4] that hydrocarbon carbonium ions are capable of hydrogen rearrangement, accompanied by shifting of the carbonium center along the carbon chain.

TABLE 2

Expt. No.	Excess density of the combustion water (in g/ml)	
	methylcyclohexanol	methylcyclohexene
1	4200	3810
2	6230	5670
3	10410	10140
4	16380	17160
5	21000	23110

So that we could make a choice between the two explanations given above, we studied the behavior of 1-methyl-1-cyclohexene under conditions that approximated those used in studying the hydrogen exchange reaction of 1-methyl-1-cyclohexanol. Here, taking into consideration the fact that water should be evolved in the dehydration of 1-methyl-1-cyclohexanol, we studied the reaction of methylcyclohexene with phosphoric acid in the presence of an

TABLE 3

Expt. No.	Substance	Relative molar amounts, substance: $D_2PO_4:D_2O$	Excess density of the substance combustion water (in g/ml)		Exchange in % of the calculated
			calculated for the exchange of all H	found	
1	1-Methyl-1-cyclohexanol	1:1,3:0	18360	10410	56.7
2	Ditto	1:2:0	17480	15520	88.8
3	1-Methyl-1-cyclohexene	1:1:1	13450	700	5.2
4*	Ditto	1:1.55:0	15540	I 4240 II 36570	27.3

* Two substances were isolated from Expt. 4: I) b.p. 101-103°, n_D^{20} 1.4488, d_4^{20} 0.8153, being a mixture of methylcyclohexenes; II) b.p. 148-150°/20 mm, n_D^{20} 1.4955, d_4^{20} 0.9528, being the dimer of the methylcyclohexenes.

As a result, a study of the hydrogen exchange reaction of 1-methyl-1-cyclohexylcarbinol with phosphoric acid revealed that the hydrocarbon carbonium ion formed in the reaction of these substances is capable of entering into hydrogen exchange with D_2PO_4 , in which connection olefins do not appear as intermediate products in the examined reaction.

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SYNTHESIS AND PROPERTIES OF SOME ESTERS OF CHLOROALKYL- PHOSPHONIC AND CHLOROALKYLDITHIOPHOSPHONIC ACIDS

E. S. Shepeleva and P. I. Sanin

(Presented by Academician A. V. Topchlev, March 7, 1956)

Certain organic compounds of chlorine (alkyl chlorides, esters of chlorostearic acid, etc.) and phosphorus (trialkyl phosphites and phosphates) are good additives for lubricating oils, greatly improving their lubrication properties. Under conditions of high frictional loads such additions lower the friction coefficient and reduce the wear of rubbing metallic surfaces. Apparently, during friction relatively high temperatures are developed at the contact points of metal surfaces, as a result of which the organic chlorine and organophosphorus compounds decompose to give the corresponding metal chlorides or phosphides, facilitating the polishing of a metal surface and the retention of an oil film [1,2].

It seemed of interest to study the chlorine-containing organophosphorus compounds as additives of the indicated type. For this purpose we prepared and studied a number of chloroalkylphosphonic and chloroalkyldithiophosphonic acid esters (see Table 1).

The chloromethyl- and β -chloroethylphosphonic acid esters were obtained by reacting the acid dichlorides with the corresponding alcohols [3-5].*

The chloromethyl- and β -chloroethyldithiophosphonic acid esters were obtained by reacting the acid dichlorides with sodium mercaptides according to the reaction:



All of the esters that we prepared are colorless liquids, readily soluble in organic solvents and insoluble in water; when added to oils they greatly improve their lubrication properties, especially their antiwear properties.

The results of studying a highly purified oil sample (viscosity 20.3 centistokes at 50°) containing the synthesized substances in a concentration of 6 mmole/100 g of oil (1.3-1.8%), are given in Table 1. A four-ball friction machine was used to make the tests.**

From the results given in the Table it follows that under the test conditions of the friction machine some of the chloromethylphosphonic acid esters increase the critical load P_c , sustained by the oil, by a factor of $1\frac{1}{2}$ - 2 without essential increase in wear. The β -chloroethylphosphonic acid esters are only slightly less active than the chloromethylphosphonic acid esters as additives. It should be mentioned that the presence of sulfur in the examined type of compounds (chloroalkyldithiophosphonic acid esters) is practically without effect on their activity. Consequently, it can be assumed that the antiwear properties of the investigated series of compounds is first of all determined by the presence of the chloroalkylphosphonyl group, containing both phosphorus and chlorine, in the studied esters.

Preparation of Dibutyl Chloromethyldithiophosphonate $\text{ClCH}_2\text{PO}(\text{SC}_4\text{H}_9)_2$. In a three-necked flask, fitted with stirrer, reflux condenser and thermometer, were put 2.3 g of finely comminuted sodium metal and 50-70 ml of dry ether and with initial cooling 9 g (0.1 mole) of butyl mercaptan was gradually added from a dropping funnel. The reaction was terminated when all of the sodium had reacted. A solution of 8.5 g (0.05 mole) of

* Also see [6-10] for the preparation of chloromethylphosphonyl dichloride.

** The tests were run by B. V. Kleimenov.

TABLE 1
Chloroalkylphosphonic and Chloroalkyldithiophosphonic Acid Esters

Substance formula	Yield in %	B.p. in °C and pressure in mm of Hg	n_D^{20}	d_4^{20}	MRD		Test results *		
					found	calcd.	ρ in kg	wear at P_c in mm (d)	maximum difference
$\text{ClCH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$	74	73-74/2	1.4175	1.4175	50.02	50.26	112	0.49	0.47
$\text{ClCH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$	64	112-113/2	1.0832	1.4120	59.29	59.50	115	0.49	0.49
$\text{ClCH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$	79	120-120/2	1.0480	1.4140	66.64	66.73	125	0.48	0.48
$\text{ClCH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$	60	122-123/8	1.1896	1.4700	49.39	49.32	102	0.50	0.52
$\text{ClCH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$	68	153-154/3	1.1411	1.5300	74.38	74.21**	120	0.52	0.37
$\text{ClCH}_2\text{PO}(\text{SC}_2\text{H}_5)_2$	47	157-158/2	1.0660	1.5230	84.42	83.45	99	0.50	0.39
$\text{ClCH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$	51	133-134/3	1.0640	1.4430	63.97	64.11	90	0.46	0.39
$\text{ClCH}_2\text{CH}_2\text{PO}(\text{OC}_2\text{H}_5)_2$	54	130-140/2	1.0144	1.4430	72.00	73.35	95	0.46	0.52
$\text{ClCH}_2\text{CH}_2\text{PO}(\text{SC}_2\text{H}_5)_2$	40	108-170/2	1.1185	1.5230	78.89	78.82	95	0.46	0.52

* P_c of the oil = 68 kg, and wear = 0.47 mm. The substance concentration in the oil was 6 mmole per 100 g of oil.

** The atomic refraction for sulfur was taken as 9.00.

chloromethylphosphonyl dichloride in dry ether was gradually added to the mercaptide obtained in this manner with cooling to 0°. Then the reaction mixture was maintained for 4 hours at room temperature, after which the flask contents were poured into a separatory funnel with a small amount of water (containing ice). The ether solution was separated and added to the subsequent extracts of the water solution. After drying the ether solution the ether was distilled off and the residue was fractionally distilled twice to give 9.0 g (66.0% of the theoretical yield) of dibutyl chloromethyldithiophosphonate. B.p. 153-154° (3 mm); d_4^{20} 1.1411; n_D^{20} 1.5300; MRD found 74.38, calculated 74.21.

Found %: P 11.53, 11.64; S 23.86, 23.93; Cl 12.82, 12.98. $\text{C}_8\text{H}_{18}\text{OPS}_2\text{Cl}$. Calculated %: P 11.27; S 23.60; Cl 12.91.

The other chloroalkyldithiophosphonic acid esters were obtained in a similar manner.

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THE INFLUENCE OF SOME ORGANOELEMENT COMPOUNDS ON THE SOLUTION RATE OF CARBON STEEL IN INORGANIC ACIDS

S. A. Balezin and M. A. Ignatyeva

(Presented by Academician S. I. Vol'kovich, January 27, 1956)

One of the primary ways of retarding the solution rate of metals in acids, and consequently, reducing hydrogen diffusion in the metal, is to use inhibitors. The inhibitors for the acid corrosion of metals, known in industrial practice as "etching additives" and "corrosion retarders", are now assuming great importance in the national economy.

Although up to 2000 different substances have been tested as acid corrosion inhibitors, only a few studies exist in which a comparison is made of the protective action shown by different inhibitors. The first review on the protective action shown by different classes of inhibitors was published by S. D. Beskov and S. A. Balezin [1]. Numerous attempts have been made to classify the known inhibitors on the basis of their chemical nature ([2-4], etc.).

Substances containing nitrogen, or phosphorus, or arsenic, or antimony, or bismuth, belong to the class of acid corrosion inhibitors. There is no information in the literature on the use of the organic compounds containing phosphorus, arsenic, antimony or bismuth as acid corrosion inhibitors.

The purpose of our study was to elucidate the influence shown by a number of organoelement compounds on the solution rate of steel in sulfuric and hydrochloric acids.*

The study was made with steel-20 in sulfuric acid solutions ranging in normality from 1 to 10, and in 1 to 5 N hydrochloric acid, at 25°. The test period lasted from 3 to 6 hours. The gravimetric study method was used the most, but we also used the volumetric and electrochemical methods.

We studied the following organoelement compounds as acid corrosion inhibitors:

- 1) tetraphenylelement bromides: $(C_6H_5)_4PBr$; $(C_6H_5)_4AsBr$; $(C_6H_5)_4SbBr$;
- 2) organophosphorus compounds: $(C_6H_5)_4PCl$; $(C_6H_5)_4PI$; $(C_6H_5)_2CH_2PI$;
- 3) diphenylelement trichlorides: $(C_6H_5)_2AsCl_3$; $(C_6H_5)_2SbCl_3$;
- 4) triphenylelement compounds: $(C_6H_5)_3N$; $(C_6H_5)_3P$; $(C_6H_5)_3As$; $(C_6H_5)_3Sb$; $(C_6H_5)_3Bi$.

From the studies made it was established that nearly all of the organoelement compounds studied by us retard the solution of steel in both sulfuric and hydrochloric acids.

Sharp inhibition of the solution rate of steel in the two mentioned acids begins at an inhibitor concentration of 0.5 mmole per liter of acid solution, which is roughly 0.02 wt. %. With further increase in the inhibitor concentration the steel solution rate shows very little change (see Fig. 1, curve for sulfuric acid).

Of the organoelement compounds studied by us the ones with the highest protective action proved to be the tetraphenylelement bromides and iodides, which at a concentration of 0.5 mmole/liter in sulfuric acid solution effect a greater reduction of the steel solution rate the higher the acid concentration. Reduction of the steel solution rate is especially noticeable in the sulfuric acid concentration range of 1 to 6N; with further

* All of the organic compounds studied by us as acid corrosion inhibitors were synthesized by us in the Institute of Organic Chemistry of the Academy of Sciences of the USSR.

Increase in the concentration of the inhibited sulfuric acid the steel solution rate remains practically constant. Thus, in 1N sulfuric acid the steel solution rate in the presence of various organoelement compounds is equal to $0.7 \text{ g/m}^2 \cdot \text{hour}$, in 5 N it is $0.2 \text{ g/m}^2 \cdot \text{hour}$, and in 10N it is a total of only $0.1 \text{ g/m}^2 \cdot \text{hour}$; in pure sulfuric acid it is: in 1N - $5.5 \text{ g/m}^2 \cdot \text{hour}$, in 5N - $11.8 \text{ g/m}^2 \cdot \text{hour}$, and in 10N - $28.0 \text{ g/m}^2 \cdot \text{hour}$.

In hydrochloric acid containing the same organoelement compounds, the steel solution rate is sharply reduced when compared with the pure acid, but in contrast to sulfuric acid, here the steel solution rate increases with increase in the hydrochloric acid concentration.

The inhibitory effect for all of the tetraphenylelement halides increases with increase in acid concentration. The most effective inhibitor of the tetraphenylelement halides proved to be tetraphenylphosphonium iodide.

The polarization curves show that the tetraphenylelement bromides and iodides influence the rate of both the cathodic and anodic processes.

We noticed that in weak sulfuric acid, inhibited with either a tetraphenylelement bromide or iodide, the steel continues to dissolve during the whole experiment (6 hours). In more concentrated sulfuric acid (5N) noticeable steel solution is observed only in the first hours of the experiment, and then it stops. Hardly any solution of the steel is observed in 8 to 10N sulfuric acid. The highly polished surface of the specimens is retained as such even after prolonged immersion (from 48 to 72 hours) in acid of this concentration.

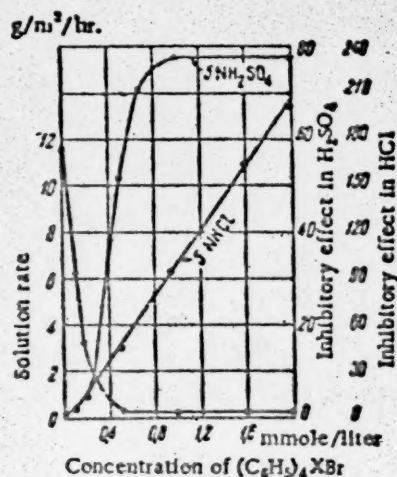


Fig. 1

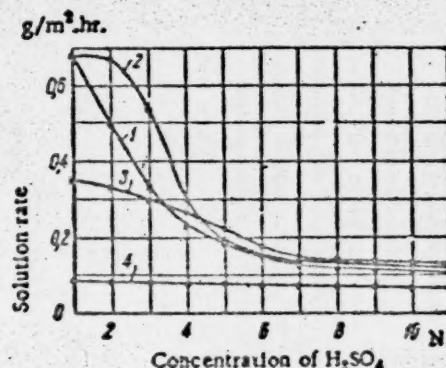


Fig. 2. Relationship between the solution rate of carbon steel and the concentration of sulfuric acid solutions in the presence of 0.5 mmole/liter of inhibitor: 1) $(\text{C}_6\text{H}_5)_4\text{PBr}$; 2) $(\text{C}_6\text{H}_5)_4\text{AsBr}$; 3) $(\text{C}_6\text{H}_5)_4\text{SbBr}$; 4) $(\text{C}_6\text{H}_5)_4\text{PI}$.

Of interest is still another fact: after being immersed in either sulfuric or hydrochloric acids that had been inhibited with either the tetraphenylelement bromides or iodides, the steel specimens become resistant to atmospheric corrosion and show a greater stability toward the pure acids than do the specimens that had not been exposed to the inhibited acids. Thus, a specimen that had been immersed for 20 hours in 10N sulfuric acid, inhibited with tetraphenylphosphonium iodide, shows 1/10 the solution rate possessed by the control specimen.

By using labeled iodine atoms we were able to show the presence of iodine on the surface of the specimens that had been immersed in acid solutions inhibited with tetraphenylphosphonium iodide. The amount of iodine on the surface of the specimens increases with increase in the sulfuric acid concentration, while in hydrochloric acid of various concentrations the amount of iodine on the surface of the specimens remains constant. Also, the amount of iodine on the surface of the specimens that had been immersed in inhibited sulfuric acid was 5-6 times the amount found on the specimens that had been immersed in inhibited hydrochloric acid.

The diphenylelement trichlorides proved to be the weakest inhibitors. In presence of these compounds the steel solution rate increases with increase in acid concentration. Their inhibitory effect in sulfuric acid of various concentration remains constant, while in hydrochloric acid it decreases with increase in acid concentration.

When studied as suspensions, the triphenylelement compounds show slight retardation of steel solution in sulfuric acid. Only triphenylphosphine and triphenylstibine retard steel solution in hydrochloric acid, while the other triphenylelement compounds accelerate the solution of steel in hydrochloric acid.

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A NEW SYNTHESIS OF ALIPHATIC AMINES

A. N. Bashkirov, Yu. B. Kagan and G. A. Kliger

(Presented by Academician A. A. Balandin, January 23, 1956)

At the present time the alkylamines are usually obtained by the reaction of alkyl halides or oxygen-containing organic compounds with ammonia, and also by the reduction of certain nitrogen-containing compounds [1,2]. The elimination of the intermediate stage in the preparation of aliphatic amines and the direct synthesis of aliphatic amines from simple chemical compounds are quite intriguing. It seemed possible that such a direct synthesis could be achieved from carbon monoxide, hydrogen and ammonia under the conditions where aliphatic oxygen-containing compounds are the primary catalytic hydrogenation products of the carbon monoxide, i.e., at high pressures and low temperatures in the presence of iron catalysts [3,4].

TABLE 1
Influence of Various Factors on the Yield of Amines in the Synthesis from Carbon Monoxide, Hydrogen and Ammonia

Temp. °C	Composition of the gas used in the syn- thesis, in %			Pressure, in atm.	Space velo- city, hour ⁻¹	Amount of amines in the synthesis products, in %
	CO	H ₂	NH ₃			
215	31.0	61.0	8.0	200	2000	7.5
					1000	10.0
					500	14.3
					200	15.0
240	28.5	57.5	14.0	60	2000	16.0
					500	25.0
240	27.0	55.0	18.0	60 120 200	2000	18.0 21.0 22.0
						3.0
						16.0
240	31.0 28.5 26.0 23.0	62.0 57.5 54.0 47.0	7.0 14.0 20.0 30.0	60	2000	18.0 20.0
						14.3
						13.0
215 235	31.0	61.0	8.0	200	500	

Data on the direct synthesis of alkylamines from carbon monoxide, hydrogen and ammonia is absent in the literature, except for the information found in the patent of A. Clark [5], according to which primary aliphatic amines are formed when the indicated gas mixture is passed over Co-ThO₂-kieselguhr catalyst at 182-221° and ~12 atm. Clark [5] indicates that activated iron and nickel catalysts are also effective here. However, data on the conditions and results of using these catalysts are not indicated in the patent.

The experiments were run in the earlier described [6] laboratory high pressure apparatus. On its way into the reactor the gas mixture (CO:H₂ = 1:2) passed through a heated autoclave containing a bubbler filled with liquid ammonia. The amount of ammonia in the starting gas mixture was regulated by heating the autoclave to the desired temperature. The experimental data were evaluated by the earlier described method [7,8].

The amount of amines in the liquid organic synthesis products was determined by their extraction from the catalyzate with 20% sulfuric acid, followed by decomposition of the resulting salts [9].

The first positive results were obtained in the experiment where the reaction conditions used were a gas mixture analyzing 31% CO, 61% H₂ and 8% NH₃, a pressure of 200 atm., a temperature of 210°, and a space velocity of the order of 2000 hr.⁻¹. The liquid synthesis products obtained under these conditions contained about 8% of amines. Thus, in principle, the direct synthesis of aliphatic amines from carbon monoxide, hydrogen and ammonia was shown to be possible.

To elucidate the conditions favorable for the synthesis of amines we studied the influence of the space

velocity, pressure, ammonia content of the starting gas mixture and temperature on their yield. The experimental results are summarized in Table 1.

The data given in Table 1 show that the yield of amines strongly depends on the space velocity and composition of the starting gas mixture. A reduction in the space velocity from 2000 to 500 hr.⁻¹ nearly doubles the yield of amines. Increasing the ammonia content in the starting gas from 7 to 30% leads to a nearly 7-fold increase in the yield of amines. The yield of amines is increased from 18 to 22% when the pressure is raised from 60 atm. to 200 atm. Variation of the temperature in the interval 215-235° is practically without effect on the amount of amines in the liquid synthesis products, which permitted us to obtain comparable data when the catalyst productivity was maintained approximately constant.

TABLE 2
Fractional Composition and Results of Analysis of the Isolated Amines

Boiling range of the fraction in °C and pressure in mm of Hg	Amount of fraction in the product, in %	Found %			Amount of amines in the fraction, in %			
		C	H	N	primary		Secondary	Tertiary
					by Van Slyke method	determined by the potentiometric titration method		
48-100	16.1	—	—	—	—	—	—	—
100-150	15.0	73.14	14.70	12.25	—	96.29	—	—
150-170/10	10.9	73.82	14.76	11.04	81.5	81.77	18.23	3.71
70-110/10	17.8	75.64	14.67	9.76	90.2	92.03	2.76	5.21
110-150/10	12.0	77.45	14.55	8.00	82.0	81.57	9.75	8.68
150-180	8.2	78.67	14.75	6.57	79.0	—	—	—
Residue	20.0	—	—	—	—	—	—	—

The amines isolated from the synthesis products were fractionally distilled and then analyzed. The data characterizing the fractional composition of the obtained amines are listed in Table 2, and also their elementary analysis results and the differential determination by the potentiometric titration [11,12] and Van Slyke [12] methods of the amino nitrogen present in the primary, secondary and tertiary amines.

The data in Table 2 show that the direct synthesis from carbon monoxide, hydrogen and ammonia, realized under the described conditions, leads predominantly to the formation of primary aliphatic amines with a variable number of carbon atoms in the chain.

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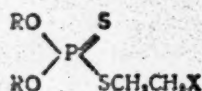
ORGANOPHOSPHORUS INSECTICIDES
O,O-DIETHYL-β-ETHYLMERCAPTOETHYLDITHIOPHOSPHATE (M-74)
AND ITS ANALOGS

Corresponding Member Acad. Sci. M. I. Kabachnik,

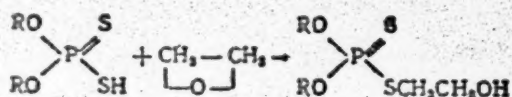
T. A. Mastryukova, M. F. Shostakovsky, E. N. Prilezhaeva, D. M. Paikin,

M. P. Shabanova and N. M. Gamper

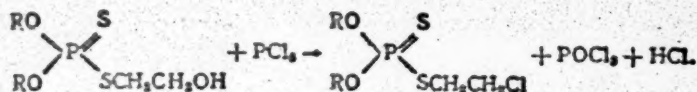
The investigations made in recent years at the Institute of Organoelement Compounds of the Academy of Sciences of the USSR and at the Plant Protection Institute of the V. I. Lenin All-Union Academy of Agricultural Sciences on the synthesis and study of the insecticidal properties of the dialkyldithiophosphoric acid derivatives have shown that highly effective insecticides can be found among the β-substituted esters of dithiophosphoric acid of the general formula



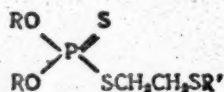
M. I. Kabachnik, T. A. Mastryukova and V. N. Odnorlova published [1] on the synthesis of some β-substituted trialkyldithiophosphates of this type, which were obtained by the reaction of ethylene oxide with dialkyldithiophosphoric acids



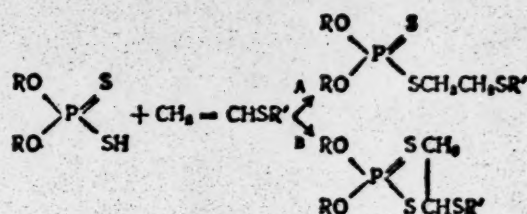
followed by rearrangement of the resulting β-hydroxyethyl derivatives, for example:



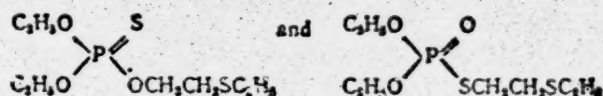
Some of these compounds proved to be effective insecticides. Having in mind the synthesis of alkylmercapto derivatives of the type



T. A. Mastryukova, E. N. Pilezhaeva, N. A. Uvarova, M. P. Skovakovsky and M. L. Kabachnik studied the addition of dialkyldithiophosphates to thiovinyl ethers [2], whose methods of preparation and properties were studied at the N. D. Zelinsky Institute of Organic Chemistry of the Academy of Sciences of the USSR [3]. However, while mercaptans add easily to thiovinyl ethers in opposition to the Markovnikov rule [4], the addition of the dialkyldithiophosphates proceeds in accord with the Markovnikov rule, and the main reaction products proves to be not the β -alkylmercaptoethyldithiophosphates (direction A), but the corresponding α -derivatives (direction B):

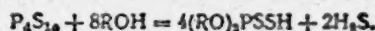


As a result, the synthesis of the mentioned β -alkylmercaptoethyl derivatives could not be accomplished by this method. However, we continued to work on this problem, since beginning with 1952 patents began to appear in print on the synthesis of this group of compounds [5], and also communications [6] on the synthesis and study of the properties of O,O-diethyl O-ethylmercaptoethylthiophosphate and its isomer - O,O-diethyl-S-ethylmercaptoethylthiophosphate

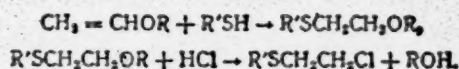


A mixture of these compounds found use as a new highly effective systemic insecticide under the name "Systox". These compounds belong to the class of β -substituted esters of monoithiophosphoric acid, i.e., they are close analogs of the above-mentioned β -alkylmercapto substituted derivatives of dithiophosphoric acid.

We realized the synthesis of the desired O,O-dialkyl- β -alkylmercaptoethyldithiophosphates by a different scheme, namely, by the reaction of β -chloroalkyl sulfides with salts of dialkyldithiophosphoric acids. The reaction went with good yields (from 70 to 94%) in most cases. The dialkyldithiophosphates needed for the synthesis were prepared by the method of L. Carius [7], which had been studied in detail by P. S. Fishchimuka [8], M. L. Kabachnik and T. A. Mastryukova [9], and other authors [10]:



The alkali salts were prepared from the dialkyldithiophosphates, which were then alkylated [9,11] with various β -chloroethylalkyl sulfides. The latter were obtained from alkyl vinyl ethers by the following scheme:



The β -alkylmercaptoethyl esters of O,O-dialkyldithiophosphoric acids prepared by this method are given in Table 1.

Even the first members of this group of compounds, studied by us as insecticides in 1953, showed high effectiveness. A more detailed study was made of the most effective member of this class of compounds, namely O,O-diethyl- β -ethylmercaptoethyldithiophosphate (Laboratory Number M-74):



Compound M-74 was studied both as a contact and as a systemic insecticide and acaricide. The substance was used as an emulsion, which was prepared from a concentrate containing 30% of M-74 and 70% of synergistic substance OP-7. The action of the preparation was studied on the harmful harlequin bug (*Eurygaster integriceps* Put.), mealy bug (*Pseudococcus maritimus* Ehrh.), circular soft scale insect (*Coccus hesperidum* L.), spider mite (*Tetranychus* sp.), red fruit mite (*Metatetranychus ulmi* Koch.), greenhouse aphid (*Myzodes persicae* Schulz.), plum aphid (*Hyaopertus pruni* F.) and grasshopper larvae (*Calliptamus italicus* L.).

TABLE 1

Formula	B. P. in °C	P in mm of Hg	n_D^{20}	d_4^{20}	Found, %				Calculated, %				Yield in %
					C	H	P	S	C	H	P	S	
1. $(C_2H_5O)_2P(S)SC_2H_5SC_2H_5$	125-126	2	1.5320	1.1445	35.4 35.1	8.9 7.0	11.6 11.9	35.1 35.2	35.0	7.0	11.3	35.1	98
2. $(C_2H_5O)_2P(S)SC_2H_5SC_2H_5$	150	1	1.5255	1.1040	40.0 40.1	7.7 7.6	10.4 10.2	—	39.7	7.7	10.2	—	78
3. $(C_2H_5O)_2P(S)SC_2H_5SCH_2CH_3$	188-190	3	1.5160	1.1050	41.8 41.6	8.0 7.9	—	—	41.6	7.9	—	—	76
4. $(i-C_4H_9O)_2P(S)SC_2H_5SC_2H_5$	134-135	3	1.5189	1.0687	40.3 40.4	7.8 7.7	9.8 10.0	31.8 31.7	39.7	7.7	10.2	31.8	80
5. $(i-C_4H_9O)_2P(S)SC_2H_5SC_2H_5$	148-149	4	1.5106	1.0622	—	—	9.5 9.3	28.9 28.0	—	—	9.4	29.1	94
6. $(i-C_4H_9O)_2P(S)SC_2H_5SCH_2CH_3$	172-173	2	1.5090	1.0687	44.5 44.5	8.4 8.6	8.3 8.2	25.8 25.9	44.9	8.3	8.2	25.7	82*
7. $(i-C_4H_9O)_2P(S)SC_2H_5SCH_2CH_3$	158-169	2	1.5053	1.0655	47.5 47.7	8.8 8.6	7.4 7.4	—	47.7	8.7	7.7	—	60*

* The lower yields were due to partial decomposition of the compounds toward the end of distillation.

To study the contact action we took thlophos (diethyl-p-nitrophenylthiophosphate) as a standard, while mercaptophos (systox) was adopted as the standard when we studied the systemic action.

Based on the data of laboratory experiments, run by the immersion method, M-74 proved to be a more toxic contact poison than thlophos for the harlequin bug. At 0.0005% concentration (active principle) M-74 caused 100% mortality of the females, while with thlophos the mortality was only 84.4%. When older larvae and adult mealy bugs were sprayed with M-74 in a concentration of 0.005% we obtained 98.5% dead and paralyzed insects, while with thlophos at the same concentration the mortality was 72.7%.

In the greenhouse experiments the spraying of ornamental plants with M-74 and with thlophos, both at a concentration of 0.05%, resulted in a mortality rate after 20 days of over 90% for the circular soft scale insect. The direct spraying of the greenhouse aphid found on the primrose with these same compounds at a concentration of 0.0025% resulted in practically complete mortality of the insects (99.9%).

The systemic action of M-74 was studied by the spray method in the field against the red fruit mite on apple trees and the plum aphid on plums, and in the greenhouse it was studied against the spider mite on roses. When used during the period of rapid multiplication of the red fruit mite both M-74 and mercaptophos at a concentration of 0.05% (based on the concentrate) were characterized by high systemic acaricidal action. When counted on the 36th day after spraying the number of mites on the apple tree was reduced to 94.6% of the original number, while for the control the number of insects had increased 10 times.

When small plum trees were sprayed with M-74 or mercaptophos in 0.05% concentration the plants were almost completely free of injurious insects in 27 days.

When these compounds were sprayed at a concentration of 0.08% on roses to control the spider mite their effectiveness lasted more than 1.5 months.

The systemic action of M-74 was also established by soaking spring wheat seed in the preparation before planting. The sprouts of such seeds proved to be toxic for both sucking (harmful harlequin bug) and gnawing (1st instar larvae of the grasshopper) insects. In the laboratory experiments M-74 in a concentration of 0.2% (active principle) effected a complete kill of grasshopper larvae and harmful harlequin bugs, feeding on 17-day old wheat sprouts. Under field conditions the use of solutions containing 0.45-0.6% (active principle) of M-74 for treating the seed gave an 84.0-96.7% kill of the harlequin bug, and in some cases complete mortality of the bugs was observed.

Consequently, M-74 is a highly effective contact and systemic insecticide and acaricide, showing much promise for the protection of agricultural plants from injurious pests.

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CATALYTIC BROMINATION OF PROPANE

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In previous investigations, made by one of us, a detailed study was made of the conditions for the catalytic chlorination of petroleum gas and its individual components for the purpose of developing commercial methods for the production of methyl chloride [1-3], carbon tetrachloride [4], hexachloroethane [5], chlorobutanes [6] and other chlorine-containing saturated hydrocarbons. As an expansion of these studies and to develop a convenient method for the synthesis of bromoalkanes we undertook a study of the catalytic bromination of alkanes.

The bromination of alkanes has been inadequately studied. Among the first studies in this field are the observations made by A. M. Butlerov [9] on the bromination of n-butane and isobutane. Among the alkanes a comparatively detailed study has been made of methane, the bromination of which is discussed in a number of patents and theoretical papers [10,11]. Data on the bromination of gases rich in methane hydrocarbons, in the presence of ferric bromide catalyst deposited on pumice, are to be found in the studies of Mihai Zapan [12]. Of theoretical interest is the work of E. Hormatz and Van Arsdalen on the photochemical and thermal bromination of neopentane [13] and other hydrocarbons [14,15].

A total of only two papers exists in the literature on the bromination of propane. B. N. Merezhkovsky [16] described the formation of the tetra-, penta- and hexabromo derivatives of propane when the latter was reacted with bromine in the presence of an iron catalyst. The use of iron as a catalyst in the bromination raises some doubt here. As is known, bromine readily reacts with iron, forming ferric bromide, which has a comparatively low melting point. The study made by Snelling [17] on the bromination of propane at elevated temperatures is of even less certain value.

We studied the bromination of the low-molecular alkanes—methane [18], ethane, propane and butane—in the presence of catalysts for the purpose of developing an efficient synthesis of the mono- and dibromoalkanes. Our data on the bromination of propane are given in this communication.

As starting material we took the technical propane fraction having the following composition: methane + ethane 0.81%, propane 91.95%, propylene 7.23%, higher 0.01%.

The experimental procedure was as follows. The propane fraction was passed through an absorption flask filled with concentrated sulfuric acid, where the unsaturated hydrocarbon impurities were removed. The propane purified in this manner was then passed through a gas meter, flow meter, calcium chloride tube, and entered the mixing flask, where bromine was added at the same time from a graduated burette. The mixing flask was immersed in a water bath, where the temperature was maintained at 80-85° by means of a temperature regulator. From the mixing chamber the bromine and propane vapors entered the catalyst tube, placed in an electric furnace. A laboratory transformer was used to maintain the temperature in the furnace at the desired level.

From the catalyst tube the reaction products entered the condensation system, composed of a coil condenser, receiver and vertical condenser. The escaping gases were freed of hydrogen bromide by absorption in water, then measured in a gas meter and collected in a gas holder. On conclusion of an experiment the wash waters were analyzed for the amount of bromine and hydrogen bromide, while the catalyzate was subjected to a detailed study. The results of some typical experiments are given in Table 1.

TABLE 1

	Experiment No.							
	1	2	4	5	6	7	8	10
A. Characterization of the Experiments								
Experimental conditions								
Temperature, °C	300	300	300	350	350	350	400	400
Mole ratio C ₃ H ₈ /Br ₂	1:0.5	1:1	1:2	1:0.5	1:1	1:2	1:0.5	1:1
Duration, hours	4	4	2	4	4	2	4	4
Gas velocity, liter/hour	10	10	10	10	10	10	10	10
Contact time	12.7	10	6.4	1.7	8.7	6.7	10.8	6
Catalyst obtained, g	73	144.5	102	65.3	149	115	61	120
Catalyst, %	1.4702	1.5612	1.7501	1.5612	1.7320	2.0252	1.6721	1.7908
n_D^{20}	1.4362	1.4810	1.5020	1.4692	1.4668	1.509	1.4700	1.4406
Bromine distribution in reaction products, %								
In catalyst	25.5	26.56	43.3	33.8	37.6	40.8	32.1	34.3
To form 1:2 by catalysis	50	50	50	50	50	50	50	50
by dehydrobromination	11.3	9	3.1	12.3	9	6.9	15.7	16
Losses	3.3	2.43	3.6	4.9	4.3	2.3	2.3	3.6
B. Fractional Distillation Results								
Initial boiling point, °C	59	59	59	59	59	59	59	59
Fraction 59-62°								
Yield %	64.2	42.9	30.8	44.8	27.6	10.8	39.6	30.4
mol. wt.	121.0	123.6	124.0	123.6	124.6	122.0	119.2	125.0
n_D^{20}	1.3163	1.3171	1.3180	1.3174	1.3175	1.3168	1.3172	1.3166
n_D^{20}	1.4288	1.4284	1.4284	1.4265	1.4285	1.4293	1.4280	1.4296
Fraction 62-113°								
Yield %	2.3	2.0	3.8	2.4	3.5	2.5	2.4	1.5
n_D^{20}	1.4680	1.4686	1.4790	1.4695	1.4785	1.4605	1.4569	1.5040
Fraction 113-116°								
Yield %	20.2	28.3	28.1	23.1	33.4	37.8	24.8	29.2
mol. wt.	200.0	198.6	198.2	199.0	195.8	193.0	202.0	201.0
n_D^{20}	1.7870	1.7908	1.7930	1.7854	1.7910	1.7880	1.7910	1.7910
n_D^{20}	1.8008	1.8001	1.8005	1.8002	1.8000	1.8000	1.8010	1.8010
Fraction 116-135°								
Yield %	2.4	1.8	1.3	3.0	3.1	3.0	3.0	1.4
n_D^{20}	1.5150	1.5160	1.5223	1.5003	1.5080	1.5091	1.5064	1.5179
Fraction 135-140°								
Yield %	3.0	15.2	23.0	19.5	10.5	7.0	10.6	14.3
mol. wt.	200.0	199.2	195.0	203.0	200.1	199.5	199.0	201.0
n_D^{20}	1.8330	1.8335	1.8370	1.8321	1.8348	1.8350	1.8310	1.8368
n_D^{20}	1.8209	1.8208	1.8280	1.8283	1.8272	1.8271	1.8270	1.8270
Residue %	7.0	12.0	11.0	14.0	29.6	37.4	18.3	21.0
Losses %	1.0	0.3	2.3	2.4	1.0	0.5	1.3	2.3

As can be seen from the data in Table 1, bromine reacts readily with propane in the presence of a catalyst at 300-400°, forming a mixture of bromopropanes.

The quantitative ratio of the mono- and dibromopropanes is found to be directly related to the ratio of the reactants and the reaction temperature. Under the investigated conditions the yield of bromopropanes is around 85-90% of the theoretical.

The physical constants of the isolated fractions are given in Table 1. The first fraction, boiling at 59-62°, corresponds to isopropyl bromide. The constants of this fraction lie close to the corresponding constants of pure isopropyl bromide (d_4^{20} 1.3138, n_D^{20} 1.4254, mol. wt. 123). Slightly high specific gravity and refractive index values for these fractions indicate the presence of small amounts of dibromopropane as impurity.

For all of the experiments the intermediate fraction (62-113°) is small and consists of mixed mono- and dibromopropanes. The fractions corresponding to dibromopropane boil at 113-116° and 135-140°. The first fraction (113-116°) is 2,2-dibromopropane, while the second (135-140°) is 1,2-dibromopropane. As can be seen from the data in Table 1, in all cases the 2,2-dibromopropane is formed in the greatest amount.

A series of experiments was run to determine the influence of the reaction temperature on the yield of the individual brominated propane derivatives. These experiments revealed that at temperatures below 300° the bromine shows incomplete reaction and even with a large excess of propane the passage of some unreacted bromine is observed. The optimum reaction temperature is 300-400°. The bromine shows complete reaction under these temperature conditions. Raising the temperature above the indicated range is accompanied by decomposition of the bromides, intensification of the dehydrobromination reaction, and more complex chemical transformations leading all the way to the formation of soot.

The reaction dependence on the temperature is illustrated by the data given in Table 2. As can be seen from the data in this table, with a propane to bromine ratio of 1:0.5 the maximum yield of monopropanes is obtained at 300°. With temperature elevation the yield of monobromopropane drops and there is a corresponding increase in the yield of mono- and dibromopropanes.

TABLE 2

Expt. No.	Ratio of components $C_3H_8:Br_2$	Temp. in °C	Amount of individual bromine derivatives in the catalyzate, in wt. %		
			Isopropyl bromide	1,2- and 2,2-dibromopropane	Polybromopropanes and soot
1	1:0.5	300	63.2	24.4	12.4
9	1:0.5	350	45.8	37.8	16.4
17	1:0.5	400	40.6	39.9	19.5
23	1:0.5	450	41.8	40.9	17.3
11	1:1	300	28.7	49.6	21.7
19	1:1	350	30.9	45.8	23.3
27	1:1	400	30.9	55.9	13.2
15	1:2	350	11.9	60.3	27.8

in the reactant mixture leads to an even sharper reduction in the isopropyl bromide yield and a corresponding increase in the total amount of di- and polybromopropanes (up to 85-90%).

By varying the ratio of the reacting components and the reaction temperature it is possible to control the yield of mono-, and di- and polybromopropane derivatives. Here it is possible to obtain a catalyzate containing up to 65% of the monosubstituted and up to 55% of the disubstituted propane.

TABLE 3

Expt. No.	Ratio of components $C_3H_8:Br_2$	Temp. in °C	Amount of individual dibromopropanes in the catalyzate, %		
			2,2-dibromopropane	1,2-dibromopropane	Ratio of 1,2- to 2,2-dibromopropane
1	1:0.5	300	15.5	7.7	1:2.0
10	1:0.5	350	24.7	12.3	1:2.0
18	1:0.5	400	26.4	13.0	1:2.0
24	1:1	300	33.9	16.2	1:2.1
20	1:1	400	33.9	14.9	1:2.3

acting components and the reaction temperature. It was established that propane brominates in the 2-position to give 2-bromopropanes and it was shown that the catalyzate contains no 1-bromopropane. With further bromination

A similar change in the character of the amount of bromopropanes as a function of the temperature is also observed for other reactant ratios, with the sole difference that an increase in the amount of bromine in the reactant mixture shifts the reaction toward the greater formation of di- and polybromopropanes. Quantitative expressions of the observed rules are readily seen from Table 2. With a propane to bromine ratio of 1:0.5 an increase in the temperature from 300 to 400° leads to a reduction in the amount of isopropyl bromide in the catalyzate from 65 to 40%, and a corresponding increase in the total amount of di- and polybromo derivatives from 35 to 60%. When the amount of bromine is increased (up to a reactant ratio of 1:1) the amount of isopropyl bromide in the catalyzate fluctuates between 40 and 30%. Here the amount of di- and polybromo derivatives approaches 60-70%. Further increase in the amount of bromine

Of great interest is the quantitative amount of individual dibromopropanes in the catalyzate, indicating the order of the bromination reaction in the paraffin series. Data on the amount of 1,2- and 2,2-dibromopropane in the catalyzate are given in Table 3. As can be seen from the data in this table, the amount of 2,2-dibromopropane is nearly twice the amount of 1,2-dibromopropane, which indicates that substitution is predominantly in the 2,2-position.

As a result, a method was developed for the catalytic bromination of propane, and conditions were found for obtaining a maximum yield of mono- and dibromopropanes.

It was shown that the composition of the obtained products is a function of the ratio of the re-

the 2-bromopropane reacts primarily at the hydrogen found on the substituted carbon atom. Here 1,2-dibromopropane is formed in lesser amount.

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THE CHEMICAL NATURE OF THE TERNARY INTERMETALLIC PHASES IN THE MAGNESIUM-COPPER-ZINC AND MAGNESIUM-COPPER-NICKEL SYSTEMS

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(Presented by Academician I. L. Chernyshev, January 24, 1956)

The ternary systems magnesium-copper-zinc and magnesium-copper-nickel have much in common from the viewpoint of the chemical properties of their components and the nature of the binary compounds— MgCu_2 , MgZn_2 and MgNi_2 , participating in the equilibrium, and appearing as members of the so-called Laves phases [1]. A study of the fusion diagrams for these systems also made it possible to establish their structural similarity.

In the middle portion of the magnesium-copper-zinc system, within the limits of phase T, formed by MgCu_2 - MgZn_2 solid solutions, there exists a ternary chemical compound with a component ratio of 1:1:1. This compound is manifested by a revealed gentle maximum of the liquidus surface, by the binary sections of phase T with magnesium and the compounds of the binary systems, and also by the presence of synclinal folds in the primary crystallization fields of magnesium [2].

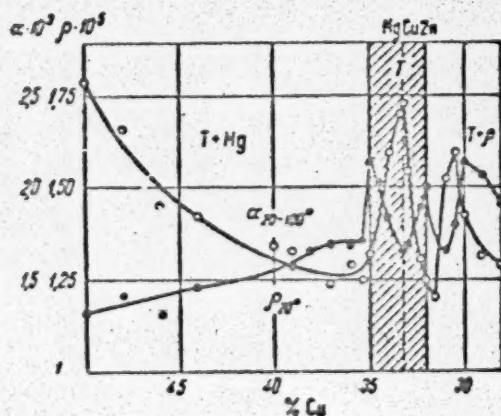


Fig. 1. Electrical resistance and its temperature coefficient along the section Mg-CuZn in the phase T crystallization region.

measurements, being rods 4 mm in diameter and 60 mm in length, were cast in a metal mold. The melting of the metals was done in a crypt furnace in corundized crucibles under a layer of flux—a eutectic mixture of barium chloride and potassium chloride. Based on the chemical analysis data the magnesium loss by burning failed to exceed 0.5-0.7% by weight.

AKL-48 low-ohmic potentiometer was used to make the electrical resistance measurements at temperatures of 25 and 100°.

At a component ratio of 1:1:1 in the system magnesium-copper-zinc the existence of compound MgCuZn in the homogeneous region of phase T is shown by a distinct minimum for the electrical resistance and a maximum for its temperature coefficient (see Fig. 1), which is in full accord with the study data obtained for all of the elements of the fusion diagram.

The formation of a continuous series of solid solutions between compounds MgCu_2 and MgNi_2 is characteristic for the ternary system magnesium-copper-nickel [3]. But taking into consideration similar rules observed in other ternary systems [2,4], and the theoretical studies dealing with the influence shown by the formation of a chemical compound on the shape of the isotherms in the field of the solvent [5], the existence of a well-defined fold for the magnesium field makes it possible to assume the existence of compound MgCuNi within the limits of the MgCu_2 - MgNi_2 solid solutions.

To verify this postulate we used one of the very sensitive methods for detecting the presence of chemical compounds in intermetallic phases, namely, the method of measuring the electrical resistance and its temperature coefficient [6].

The specimens for the electrical resistance

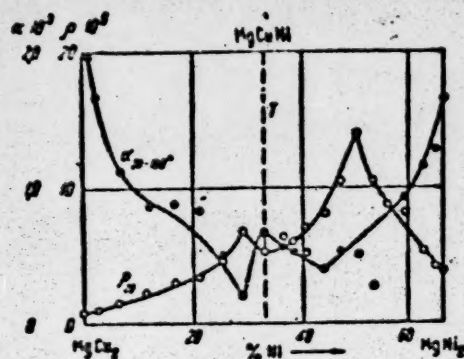


Fig. 2. Electrical resistance and its temperature coefficient along the section $\text{MgCu}_2 - \text{MgZn}_3$.

The curve for the temperature coefficient of the electrical resistance is adiabatic to the electrical resistance curve and possesses a corresponding gentle maximum at the same component ratio.

A comparison of the obtained results with the study data obtained for the fusion diagrams of ternary systems enables us to regard the T phases of these systems as being ternary berthollides, i.e., as phases that contain the compounds MgCuZn and MgCuNi either in a state of dissociation [7] or in a state of changed valences for the components [8]. The first compound is relatively more stable than the second.

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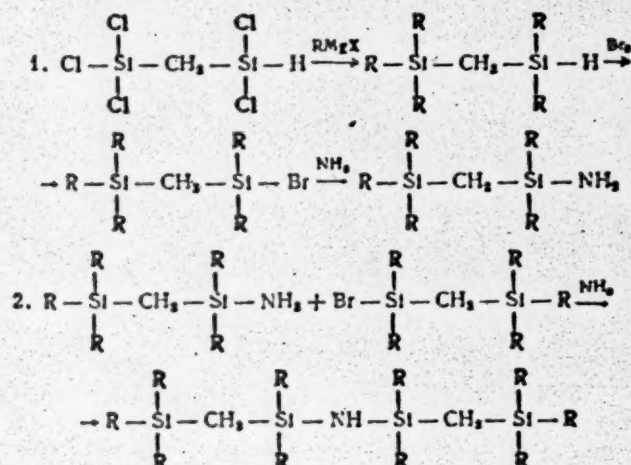
* T.p. = C. B. Translation pagination.

SYNTHESIS OF COMPOUNDS WITH SILAZINE LINKS

N. S. Nametkin, Academician A. V. Topchiev, L. S. Povarov and G. V. Garnishevskaya

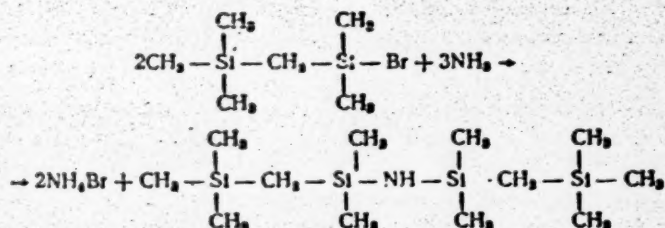
In previous communications [1-3] we had shown the possibility of using pentachlorodisilanomethane—a reaction product of methylene chloride with silicon—to obtain compounds with siloxanocarbon links ($-\text{Si}-\text{CH}_2-\text{Si}-\text{O}-\text{Si}-\text{CH}_2-\text{Si}-$) through the corresponding silicohydrocarbons of the pentaalkyldisilanomethane series.

In the present study we have shown the possibility of using pentachlorodisilanomethane to synthesize compounds with both silicocarbon and silazine links ($-\text{Si}-\text{CH}_2-\text{Si}-\text{NH}-\text{Si}-\text{CH}_2-\text{Si}-$) by the following general schemes:



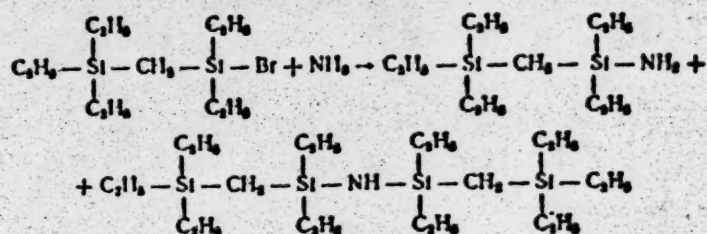
The pentaalkylbromo derivatives of disilanomethane are obtained when the pentaalkyl derivatives [1-3] of disilanomethane are reacted with bromine.

The reaction of pentamethylbromodisilanomethane with ammonia gave us bis(pentamethyldisilanomethane) amine, formed according to the scheme:

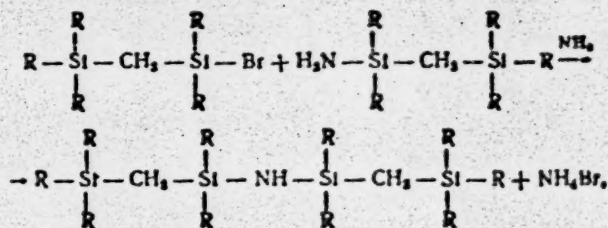


The primary amine (pentamethyldisilanomethaneamine) was not found in the reaction products.

The reaction of pentaethylbromodisilanomethane with ammonia gave the primary amine and some secondary amine by the scheme:



The reaction of either pentapropylbromodisilanomethane or pentabutylbromodisilanomethane with ammonia gave only primary amines, and secondary amines were not found in the reaction products. The latter were obtained by reacting the pentaalkylbromo derivatives of disilanomethane with primary amines and subsequent treatment of the reaction products with ammonia by the scheme:



where $\text{R} = \text{C}_2\text{H}_5; \text{C}_3\text{H}_7; \text{C}_4\text{H}_9$.

EXPERIMENTAL

Preparation of Pentaalkylbromo Derivatives of Disilanomethane. Bromine was added at 5-10° to the corresponding pentaalkyl derivatives of disilanomethane, contained in a three-necked flask, fitted with reflux condenser, dropping funnel and tube for nitrogen passage. Toward the end of bromine addition the temperature was raised to 60-80°. On conclusion of bromine addition a stream of nitrogen was passed through the flask to remove hydrogen bromide and excess bromine, after which the product was distilled.

The properties of the obtained pentaalkylbromo derivatives of disilanomethane are listed in Table 1.

Preparation of Pentaalkyldisilanomethaneamines and Bis(pentaalkyldisilanomethane)amines. All the nitrogen-containing silicoorganic compounds described by us were prepared in a flask fitted with a reflux condenser and a tube for the admittance of ammonia.

Bis(pentamethyldisilanomethane)amine, pentaethyldisilanomethaneamine, pentapropyldisilanomethaneamine and pentabutyldisilanomethaneamine were obtained by reacting dry gaseous ammonia with the corresponding pentaalkylbromo derivatives of disilanomethane in either ether or toluene at the boiling point of the reaction mixture.

Bis(pentaethyldisilanomethane)amine, bis(pentapropyldisilanomethane)amine and bis(pentabutyldisilanomethane)amine were obtained by reacting the corresponding pentaalkylbromo derivatives of disilanomethane with pentaalkyldisilanomethaneamines in toluene. The reaction mixture was heated at the boil, and when all of the hydrobromide salt of the corresponding amine had precipitated, the mixture was treated with dry ammonia. On conclusion of reaction the ammonium bromide precipitate was filtered, and the liquid reaction products were fractionally distilled.

Preparation of Bis(pentamethyldisilanomethane)amine. Ammonia was passed for 20 hours through a solution

TABLE 1

Compound	Formula	B.p. in °C and pressure in mm Hg	n_D^{20}	n_D^{25}	Fr. %		MR _D		Yield in %
					found	calcd.	found	calcd.	
Pentamethylbromodisilanomethane	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3 - \text{Si} - \text{CH}_2 - \text{Si} - \text{Br} \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	170/750	1.0840	1.4547	35.45 35.30	35.55	56.30	56.43	88.8
Pentaethylbromodisilanomethane	$\begin{array}{c} \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \\ \quad \\ \text{C}_2\text{H}_5 - \text{Si} - \text{CH}_2 - \text{Si} - \text{Br} \\ \quad \\ \text{C}_2\text{H}_5 \quad \text{C}_2\text{H}_5 \end{array}$	112/3	1.0757	1.4828	26.85 26.00	27.07	79.33	79.58	90.4
Pentapropylbromodisilanomethane	$\begin{array}{c} \text{C}_3\text{H}_7 \quad \text{C}_3\text{H}_7 \\ \quad \\ \text{C}_3\text{H}_7 - \text{Si} - \text{CH}_2 - \text{Si} - \text{Br} \\ \quad \\ \text{C}_3\text{H}_7 \quad \text{C}_3\text{H}_7 \end{array}$	131— 132/1.0	1.0021	1.4752	21.40 22.30	21.95	102.94	102.73	87.7
Pentabutylbromodisilanomethane	$\begin{array}{c} \text{C}_4\text{H}_9 \quad \text{C}_4\text{H}_9 \\ \quad \\ \text{C}_4\text{H}_9 - \text{Si} - \text{CH}_2 - \text{Si} - \text{Br} \\ \quad \\ \text{C}_4\text{H}_9 \quad \text{C}_4\text{H}_9 \end{array}$	179— 180/1.5	0.9667	1.4748	17.70 17.79	16.32	126.87	125.88	91.6

of 67.59 g (0.3 mole) of pentamethylbromodisilanomethane in 200 ml of ether. The yield of bis(pentamethyldisilanomethane)amine was 42 g (34.5% yield). B.p. 93° at 2 mm.

Found %: C 47.21, 47.38; H 11.64, 11.64; N 4.49, 4.47. $\text{C}_{12}\text{H}_{23}\text{NSi}_4$. Calculated %: C 47.16; H 11.55; N 4.58. Mol. wt. found 299, 301; for $\text{C}_{12}\text{H}_{23}\text{NSi}_4$ Calculated 305.6.

Preparation of Pentaethyldisilanomethaneamine. Ammonia was passed for 15 hours through a solution of 85 g (0.28 mole) of pentaethylbromodisilanomethane in 200 ml of toluene. The yield of pentaethyldisilanomethaneamine was 35.4 g (61.8%). B.p. 105° at 6 mm.

Found %: C 57.15, 57.23; H 12.84, 12.90; N 5.97, 5.94. $\text{C}_{11}\text{H}_{23}\text{NSi}_4$. Calculated %: C 57.01; H 12.67; N 6.05.

In addition to the pentaethyldisilanomethaneamine, we isolated a product with b.p. 188° at 2 mm, corresponding to the bis(pentaethyldisilanomethane)amine. The yield was 13 g (22.8%).

Preparation of Bis(pentaethyldisilanomethane)amine. To 27 g (0.12 mole) of pentaethyldisilanomethaneamine was added 35.4 g (0.12 mole) of pentaethylbromodisilanomethane and 100 ml of toluene. The mixture was heated at the boil for 10 hours, after which ammonia was passed through it for 10 hours. The yield of bis(pentaethyldisilanomethane)amine was 31.9 g (60%). B.p. 188° at 2 mm.

Found %: C 59.36, 59.52; H 12.64, 12.65; N 2.83, 2.82. $\text{C}_{22}\text{H}_{43}\text{NSi}_4$. Calculated %: C 59.25; H 12.43; N 3.16. Mol. wt. found 436, 446; for $\text{C}_{22}\text{H}_{43}\text{NSi}_4$ Calculated 445.9.

Preparation of Pentapropyldisilanomethaneamine. Ammonia was passed for 20 hours through a solution of 81.6 g (0.22 mole) of pentapropylbromodisilanomethane in 200 ml. of toluene. The yield of pentapropyldisilanomethaneamine was 61.2 g (72.8%). B.p. 132° at 3 mm.

Found %: C 63.90, 63.91; H 13.01, 13.05; N 4.47, 4.56. $\text{C}_{19}\text{H}_{33}\text{NSi}_4$. Calculated %: C 63.74; H 13.04; N 4.65.

Preparation of Bis(pentapropyldisilanomethane)amine. To 41 g (0.14 mole) of pentapropyldisilanomethaneamine in 100 ml of toluene was added 60 g (0.14 mole) of pentapropylbromodisilanomethane. The mixture was heated at the boil for 15 hours, after which ammonia was passed through it for 10 hours. The yield of bis(pentapropyldisilanomethane)amine was 41.5 g (50%). B.p. 214–216° at 2.5 mm.

Found %: C 65.84, 65.95; H 12.87, 12.99; N 2.14, 2.13. $\text{C}_{32}\text{H}_{75}\text{NSi}_4$. Calculated %: C 65.56; H 12.90; N 2.39. Mol. wt. found 565, 586; for $\text{C}_{32}\text{H}_{75}\text{NSi}_4$ Calculated 586.2.

Preparation of Pentabutyldisilanomethaneamine. Ammonia was passed for 30 hours through a solution of

TABLE 2

Compound	Formula	B.p. °C, pressure (mm Hg)	n_D^{20}	n_D^{25}	MRD	
					found	calcd.
Pentaethylidisilanomethane- amine	$(C_2H_5)_2Si-CH_3-Si(C_2H_5)_2NH_2$	105/0	0.8574	1.4033	74.32	74.40
Pentapropylidisilanomethane- amine	$(C_3H_7)_2Si-CH_3-Si(C_3H_7)_2NH_2$	133/3	0.8480	1.4010	97.50	98.15
Pentabutylidisilanomethane- amine	$(C_4H_9)_2Si-CH_3-Si(C_4H_9)_2NH_2$	174/3	0.8435	1.4038	121.30	121.55
Bis(pentamethylidisilano- methane)amine	$[(CH_3)_5Si-CH_3-Si(CH_3)_5NH_2]$	93/2	0.8352	1.4478	97.90	98.27
Bis(pentaethylidisilano- methane)amine	$[(C_2H_5)_5Si-CH_3-Si(C_2H_5)_5NH_2]$	188/2	0.8500	1.4809	142.79	143.37
Bis(pentapropylidisilano- methane)amine	$[(C_3H_7)_5Si-CH_3-Si(C_3H_7)_5NH_2]$	214— 216/2.5	0.8641	1.4725	191.38	190.87
Bis(pentabutylidisilano- methane)amine	$[(C_4H_9)_5Si-CH_3-Si(C_4H_9)_5NH_2]$	257— 257/3.5	0.8622	1.4731	236.38	237.17

88 g (0.2 mole) of pentabutylbromodisilanomethane in 150 ml of toluene. The yield of pentabutylidisilanomethane-amine was 60 g (80.7%). B.p. 174° at 3 mm.

Found %: C 67.74, 67.90; H 13.35, 13.25; N 3.62, 3.70. $C_{22}H_{48}NSi_2$. Calculated %: C 67.86; H 13.29; N 3.77.

Preparation of Bis(pentabutylidisilanomethane)amine. To 30 g (0.08 mole) of pentabutylidisilanomethaneamine in 150 ml of toluene was added 15.6 g (0.03 mole) of pentabutylbromodisilanomethane. The mixture was heated at the boil for 15 hours, after which ammonia was passed through it for 10 hours. The yield of bis(pentabutylidisilanomethane)amine was 12 g (50%). B.p. 255-275° at 3.5 mm.

Found %: C 69.27, 29.29; H 12.87, 12.99; N 1.68, 1.70. $C_{42}H_{92}NSi_4$. Calculated %: C 69.44; H 13.18; N 1.93. Mol. wt. found 696, 712; for $C_{42}H_{92}NSi_4$. Calculated 726.4.

The properties of the nitrogen-containing silicoorganic compounds obtained by us are given in Table 2.

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SYNTHESIS OF HIGHER $\alpha,\alpha,\alpha,\omega$ -TETRACHLOROALKANES AND 1,1,1-TRICHLOROALKANES

Academician A. N. Nesmeyanov, Sh. A. Karapetyan and R. Kh. Freidlina

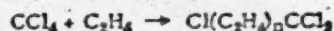
The telomerization of ethylene with either carbon tetrachloride or chloroform yields a mixture of polychloroalkanes having the structure $X(C_2H_2)_nCCl_3$, where $X = H$ or Cl . Compounds having $n = 1-7$ were isolated from a mixture of $\alpha,\alpha,\alpha,\omega$ -tetrachloroalkanes, and the amount of components with $n = 1-4$ was studied as a function of pressure [1,2]. Compounds having $n = 1-5$ were isolated from a mixture of 1,1,1-trichloroalkanes, but here the influence of the reaction conditions on the composition was not studied [3].

An increase in the pressure and in the relative concentration of ethylene favors the formation of higher products. Consequently, to increase the amount of higher tetrachloroalkanes, Joyce and coworkers [1] either substantially increased the pressure or added solvents.

G. D. Efremova and G. G. Leontyeva [4] showed that at 90-100° and pressures above 100 atm. the system $C_2H_4-CCl_4$ is homogeneous for all $C_2H_4:CCl_4$ ratios. Consequently, the pressure does not simultaneously give both the ethylene concentration and the composition of the reaction products.

We studied the separate influence of relative ethylene concentration and pressure on the composition of the telomerization reaction products and showed that it is possible to synthesize the higher chloroalkanes at pressures of 100-150 atm.

TABLE 1



Expt. No.	Charge		Pressure, atm.	conversion, CCl_4 , %	Composition of mixed tetrachloroalkanes, %		
	CCl_4 moles	C_2H_4 mole/mole			C_2	C_3	$C_{>3}$
1	2.5*	1.6	100	37	64	20	7
2	1.5**	1.8	200	35	60	19	11
3	4	5	110	64	37	30	31
4	3.6	5.3	200	67	19	22	59
5	2.0	6.5	110	69	33	27	39
6	3.1	6.2	130	53	29	28	45
7	3.1	6.1	140	68	25	28	49
8	3.1	6.9	150	70	21	21	58
9	1.0	14	100	77	30	28	42
10	1.75	13	150	59	14	19	67
11	1.0	20	150	58	9	12	79
12	0.5	27	100	80	19	20	61
13	0.5	40	150	38	3	3	84

* 100 ml of water was added.

** 250 ml of water was added.

EXPERIMENTAL METHOD

The experiments were run in rotating autoclaves having a capacity of 0.5-2.7 liters. The initiator was isobutyric acid azodinitrile, taken in a concentration of 0.8-1 g per liter of autoclave capacity. The amounts of reacted ethylene and CCl_4 (percent conversion) were calculated from the weight and composition of the chloroalkane mixture. The ethylene failing to react was measured in a gas meter. The pressures were maintained by pumping ethylene into the autoclave. The initial ethylene concentration is indicated in the tables.

The high heat effect, the presence of an induction period, and at times the violent (with a tendency to explode) course of the reaction [5], were the reasons for the 2-5% fluctuation in the pressure and temperature. The reaction temperature was 90°, and the time was 4-5 hours.

The chloroalkane mixtures were fractionally distilled through a column in vacuo. The constants of the components corresponded to those described earlier [1-3].

EXPERIMENTAL RESULTS AND DISCUSSION

The experiments with CCl_4 run in the homogeneous region, are summarized in Table 1. The data for CHCl_3 are shown in Table 2. From Table 2 (Expt. Nos. 3-6) it can be seen that the trichloroalkane composition at low pressures shows hardly any change when the amount of ethylene is increased 2.5-3.5 times at constant pressure, while at 100 atm. (Expt. Nos. 7-10) an increase in the ethylene charge results in a corresponding increase in the amount of higher products. From this it can be concluded that critical phenomena are present in the $\text{CHCl}_3\text{-C}_2\text{H}_4$ system.

TABLE 2



Expt. No.	Charge		Pressure, atm.	Conversion, % CHCl ₃	Composition of mixed trichloroalkanes, %					
	CHCl ₃ , moles	C ₂ H ₄ , mole/mole			C ₁	C ₂	C ₃	C ₄	C ₅	C ₆
1	2.5	0.3	10	5	50	34	16	—	—	—
2	0.75	1.6	13	18	35	40	25	—	—	—
3	1.5	2	25	40	21	51	28	2	—	—
4	0.5	7	25	35	19	53	23	5	—	—
5	3	2.3	50	48	10	38	27	17	8	—
6	1	5.7	50	63	12	30	25	19	10	4
7	8	3.5	100	49	4	24	25	16	14	17
8	2.1	7.7	100	49	3	16	19	19	14	29
9	1.1	13	100	57	2	10	17	16	18	37
10	0.6	24	100	48	—	7	10	9	8	66
11	9	1.7	160	38	4	28	24	18	13	14
12	3.2	7.1	160	51	—	8	14	13	11	54

From the data in Table 1 two families of curves for the tetrachloroalkanes are plotted in Figs. 1 and 2. Fig. 3, constructed from the data given in Table 2, shows that the rules for the change in trichloroalkane composition are the same as for the tetrachloroalkanes—the amount of each component passes through a maximum. It can be seen from Fig. 4 that the observed maximum amount of the individual components drops rapidly with increase in the number of carbon atoms in the molecule, reaching a value of 4-7% for tetrachloropentadecane, in which connection the absolute maximum values are approximately the same for both the tetra- and trichloroalkanes.

It follows from the curves shown in Figs. 1-3 that the relative ethylene concentration C_2 and pressure P exert approximately the same degree of influence on the polychloroalkane composition. Thus, for example, the yield of higher ($C_{>7}$) tetrachloroalkanes at a pressure of 150 atm. and $C_2 = 40$ mole/mole is as high as 95%.

After removing the tetrachloropentadecane by distillation, the tetrachloroalkane mixtures from Expt. Nos. 11 and 13 were separated into a series of fractions on the basis of their solubility in CCl_4 and acetone. The C, H and Cl analyses revealed that these fractions correspond to the formula $\text{C}_n\text{H}_{2n-2}\text{Cl}_4$. The average molecular weight of these fractions, representing 55-75% of the total amount of chloroalkanes, was 420-840, and the average number of carbon atoms was correspondingly 20-50.

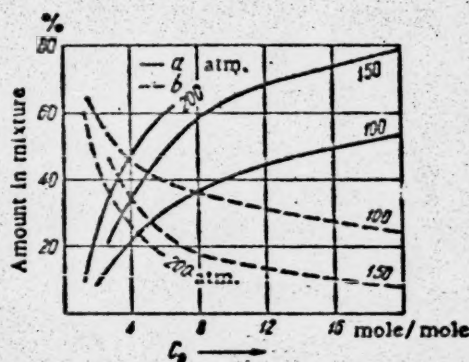


Fig. 1. Influence of the relative ethylene concentration C_2 (in moles per mole of CCl_4) on the tetrachloroalkane composition. a) Higher tetrachloroalkanes $C_{>7}$; b) tetrachloropentadecane.

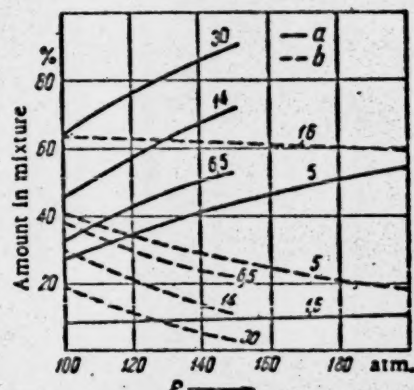


Fig. 2. Influence of pressure P on the tetrachloroalkane composition. The figures on the curves denote the relative ethylene concentration C_2 (in moles per mole of CCl_4). a) Higher tetrachloroalkanes $C_{>7}$; b) tetrachloropentadecane.

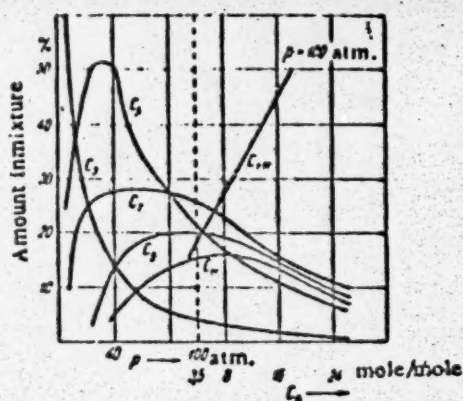


Fig. 3. Influence of pressure and relative ethylene concentration on the trichloroalkane composition.

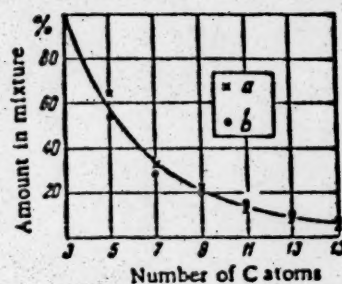


Fig. 4. Maximum amount of individual components in the polychloroalkane mixture. a) Tetrachloroalkanes; b) trichloroalkanes.

TABLE 3

	B.p., °C. 0.3 mm Hg	d_4^{20}	n_D^{20}	MR		Found %			Calculated %		
				found	calcd.	C	H	Cl	C	H	Cl
C_{13}	103—108	1.0339	1.4649	76.94	76.84	54.34 54.50	8.82 8.79	37.29 37.07	54.28	8.76	36.97
C_{15}	123—125	1.0142	1.4658	86.18	86.07	57.00 56.80	9.11 9.02	33.64 33.89	57.06	9.25	33.69
C_{17}	138—143	0.9992	1.4663	95.32	95.30	59.14 59.22	9.55 9.51	31.30 31.11	59.38	9.61	30.95

From the mixed trichloroalkanes we isolated 1,1,1-trichlorotridecane (C_{13}), 1,1,1-trichloropentadecane (C_{15}) and 1,1,1-trichloroheptadecane (C_{17}), the constants and analysis of which are given in Table 3.

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RECRYSTALLIZATION DIAGRAM OF CHROMIUM

E. M. Savitsky, V. F. Terekhova and A. V. Kholopov

(Presented by Academician L. P. Barbina, February 21, 1956)

Recrystallization diagrams, linking metal grain size with deformation degree and temperature, are of great importance in establishing the optimum conditions for the pressure molding and annealing of semifabricates and parts from metals and alloys. Some statements exist in the literature on the influence shown by the recrystallization process on the plastic properties of chromium [1,2], but no recrystallization diagram for chromium has been published.



Fig. 1. Microphotographs of chromium specimens, 100 \times . a) Original structure, annealed after casting at 1200°; b) 2.5% deformation, annealed at 1020°; c) 2.5% deformation, annealed at 1500°; d) 40% deformation; e) 40% deformation, annealed at 1020°; f) 40% deformation, annealed at 1500°.

In the present study a type I recrystallization diagram was constructed for remelted electrolytic chromium, which at the present time is the purest commercial form of chromium. A chemical analysis of the electrolytic chromium, refined in a hydrogen atmosphere at 1350° for 70-100 hours under technical conditions, gave the following average results (in%): Cr 99.5; N 0.1; C 0.01 - 0.04; Si 0.05; Fe 0.1; Ni 0.1; O₂ 0.005.

We ran the chromium fusion in a vacuum high-frequency furnace in zirconium oxide crucibles with casting in a copper mold. The specimens after casting were turned to obtain a pure surface and remove the outer layer, which showed slight copper contamination. The starting specimens had a diameter of 11 mm and a length of 10 mm. To remove internal stresses the specimens were annealed at 1100-1200° for 1-2 hours.

The cast and annealed specimens had fairly uniform fine-grained structure with an average grain size of about 0.01 mm² (Fig. 1a). The microhardness of the cast specimens was 120-140 kg/mm². Under unidirectional stress at room temperature, such specimens showed up to 35-40% deformation resistance without the formation of cracks. The compression was run on a hydraulic press with reduction gears at a rate of 2-4 mm/min. The following deformation values (relative contraction values under stress) were chosen: 2.5; 7.5; 10; 12.5; 15; 20; 25; 30 and 40%. Crushing of the grains was observed when the degree of deformation was increased. The deformation texture is very distinct at 40% (Fig. 1, d, f).

After the final deformation the specimens were annealed in evacuated quartz ampoules for 2 hours at



Fig. 2. X-ray patterns of chromium specimens. a) Original cast and annealed specimen; b) 40% deformation, annealed at 950°; c) 40% deformation, annealed at 1020°.

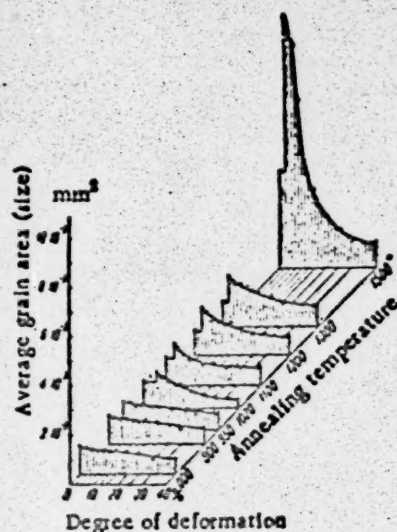


Fig. 3. Recrystallization diagram of chromium.

The etching of the specimens was done in concentrated hydrochloric acid, and the method of electrolytic etching in 10% oxalic acid was also used. Two methods were used to calculate the grain size: comparison with a standard scale and calculation of the grain area under the microscope.

The debyeograms of the specimens were taken using molybdenum radiation and an exposure of 1 hour. The hardened surface layer was removed by etching in hydrochloric acid.

The microstructures and x-ray patterns of the cast, deformed, and recrystallized chromium specimens are shown in Figs. 1 and 2.

A reduction in the microhardness of chromium grains begins after annealing from 800°, which may be associated with reversion phenomena (see Table 1).

It was established by the x-ray method that in the chromium specimens, deformed by 40%, recrystallization begins at 950-980° (see Fig. 2). From the recrystallization diagram constructed for chromium (see Fig. 3) it can be seen that complete recrystallization of the specimens occurs at 1020°. The magnitude of the critical degree of deformation at 1020° is 7%; at 1200° it is 5%, and at 1500° it reduces to 2.5%. At 1020° a reduction in grain size is observed under large deformations. This is due to the formation of new grains. Similar phenomena have been observed for aluminum-magnesium alloys for certain steels, and for pure magnesium [3,4].

TABLE 1

Change in microhardness (in kg/mm²) as a function of deformation and annealing temperature

Annealing temperature in °C	Deformation in %						
	5	10	15	20	25	30	40
20	150	150	155	155	165	185	190
700	150	150	150	155	160	190	190
800	150	150	145	140	135	135	—
1020	110	110	110	110	110	110	110

the temperatures: 200; 500; 700; 800; 900; 950; 980; 1020; 1100; 1200; 1300°, and in hydrogen at 1500°. A platinum-platinum rhodium thermocouple was used to control the annealing temperature with an accuracy of $\pm 5^\circ$. The annealed specimens were subjected to microscopic and x-ray studies, and also to microhardness measurement.

The growth of new grains proceeds with elevation of the temperature above 1020° and the stage of collective recrystallization begins, but the grain growth is very small up to an annealing temperature of 1300°. Substantial grain growth occurs at 1500°.

As a result, recrystallization in chromium proceeds by two paths. At low degrees of deformation an increase in temperature leads only to coarser crystals due to combination of the old crystals with each other (collective recrystallization). This recrystallization path is typical for regions of critical deformation values (Fig. 1, b, c, d). At large deformation values the recrystallization proceeds at first with the appearance and growth of new grains (work recrystallization) and only after that by the collective recrystallization path (Fig. 1, e, f).

The constructed diagram makes it possible to determine the change in crystal structure as a function of the annealing temperature and degree of cold deformation, and also to select the optimum conditions for the annealing of chromium. The diagram can also be used to study the nature of chromium brittleness.

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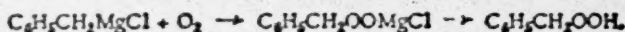
LIQUID PHASE OXIDATION OF ALIPHATO-AROMATIC HYDROCARBONS WITH OXYGEN GAS. TOLUENE HYDROPEROXIDE

P. G. Sergeev and V. V. Fedurova

Presented by Academician B. A. Kazansky, March 12, 1956

The formation of the hydroperoxide when toluene is reacted with oxygen at temperatures around 100° has been mentioned by a number of authors [1-3]. However, the amount of hydroperoxide present in the oxidized toluene was so small that all attempts to isolate it in the free state proved unsuccessful and caused investigators to reject its preparation by this method.

Toluene hydroperoxide was described by Walling and Buckler [4], who obtained it by reacting benzylmagnesium chloride with oxygen-saturated ether at -75°, in accord with the reaction



The hydroperoxide obtained in this manner was 90% pure, b.p. 53.5° (0.09 mm), n_D^{20} 1.5352 and d_4^{20} 1.120.

We oxidized toluene with atmospheric oxygen at a temperature of 110° and in the presence of small amounts of manganese resinate as catalyst. We used crystalline isopropylbenzene peroxide ($C_6H_5C(CH_3)_2O_2$) as the oxidation initiator. The amount of hydroperoxide, determined iodometrically, was very small and after 44 hours of oxidation did not exceed 0.6%, and with further oxidation it decreased. Along with the hydroperoxide, both benzaldehyde and benzoic acid were found in the oxidized toluene. Of the three products the benzaldehyde was present in predominant amount.

Isolation of the hydroperoxide was based on its ability to yield water-soluble salts when reacted with dilute alkali solutions. Treatment of the oxidized toluene with 21% sodium hydroxide solution and subsequent decomposition of the resulting sodium salt with carbon dioxide gas gave a product with a hydroperoxide content of 68.8% and n_D^{20} 1.5322. Here up to 50% of the original hydroperoxide was lost due to decomposition during isolation. When the concentrated toluene hydroperoxide preparations were stored under ordinary conditions for approximately 6 months they underwent complete decomposition with the formation of benzaldehyde as the main product.

EXPERIMENTAL

The toluene used for the oxidations was first washed with sulfuric acid (d 1.84), then with water, 10% sodium hydroxide solution, and again with water. The dried toluene was distilled through a Vigreux column and had the following constants: boiling range (determined by the Kremer-Shpliker method) 109.6-111.2°, d_4^{20} 0.864, n_D^{20} 1.4965, bromine number 0.0096.

Into a cylindrical glass flask, expanded in the upper portion and fitted with a reflux condenser, thermometer, stirrer and capillary for admitting air, was charged 350 ml of toluene, manganese resinate (2.5 m.g per mole) and 70 mg. of isopropylbenzene peroxide. The temperature of the mass was raised to 110°, after which dry air was passed through the system at a rate of 10 liters per hour. Samples were removed at periodical intervals to determine the amount of hydroperoxide. After 44 hours of oxidation the hydroperoxide content reached 0.6%.

Isolation of Benzaldehyde. A sample (0.37 g) of oxidized toluene containing 0.3% of the hydroperoxide was dissolved in 10 ml of alcohol. To decompose the hydroperoxide the solution was treated with 5 ml of 20% sodium bisulfite solution.



To the mixture after vigorous shaking was added 150 ml of a hydrochloric acid solution of 2,4-dinitrophenylhydrazine (1 g of substance in 1 liter of 2N HCl), after which the solution was shaken vigorously and allowed to stand for 10-12 hours. The yellow benzaldehyde 2,4-dinitrophenylhydrazone precipitate was filtered through a porous filter No. 3, washed with 2N HCl, then with water, and dried at 110°. The yield calculated as benzaldehyde was 0.0024 g. The product had m.p. 233° (determined on a Berl block); from the literature [5], m.p. 237°.

Isolation of Benzoic Acid. 700 ml of oxidized toluene was washed with 5% sodium bicarbonate solution. Evaporation and acidification of the wash waters gave 1.1 g of white crystals. After recrystallization from water, m.p. 120°. The mixed melting point with authentic benzoic acid failed to be depressed.

Isolation of the Hydroperoxide. 700 ml of oxidized toluene was washed with 5% NaHCO₃ solution, then with water, and dried over fused potash. The product remaining after distilling off the unchanged toluene at 20-21° (12 mm) was treated under cooling with 9 ml of 21% NaOH solution, after which the alkaline water layer was separated and carbon dioxide gas was passed through it. The oil that separated here was extracted with ether, the removal of which by evaporation gave as residue 2.22 g of light-yellow product with a hydroperoxide content of 31.5%. After repeating the alkali treatment and all of the other operations we obtained about 1 g of colorless viscous liquid with an almond odor. Iodometric analysis of this material showed the presence of 68.8% of the hydroperoxide, n_D^{25} 1.5322.

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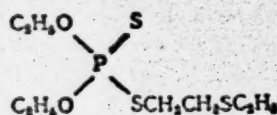
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ORGANOPHOSPHORUS COMPOUNDS

SOME ANALOGS OF O,O-DIETHYL-β-ETHYLMERCAPTOETHYLDITHIOPHOSPHATE (M-74), LESS TOXIC FOR WARM-BLOODED ANIMALS

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Together with M. F. Shostakovsky and E. N. Filizhaeva [1], we recently published a paper on the synthesis and study of the insecticidal properties of O,O-diethyl-β-ethylmercaptoethylthiophosphate (M-74) and some of its analogs. These compounds proved to be highly active insecticides and acaricides, showing both contact and systemic action.



Among these compounds the most active proved to be M-74 itself. In many cases its contact action exceeded that of thiophos (O,O-diethyl-p-nitrophenylthiophosphate); in its systemic action it was equal to mercaptophos (a mixture of isomeric O,O-diethyl-β-ethylmercaptoethylthiophosphates), and in some cases it even exceeded it.

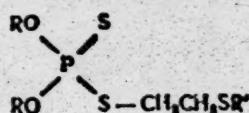
A study of the toxic properties of M-74 with respect to warm-blooded animals revealed that this substance possesses comparatively high toxicity, although it is less toxic, for example, than isomercaptophos (Isosystox). Thus, when introduced intravenously in rabbits the LD₅₀ for M-74 is equal to 3.0-3.5 mg per kg of body weight, while for Isosystox it is 2-2.5 mg/kg.

Consequently, the purpose of our further studies was to synthesize such analogs of M-74 as, being equal to it in insecticidal activity, would be less toxic for warm-blooded animals.

Several statements exist in the literature that derivatives of the methyl esters of thiophosphoric and dithiophosphoric acid frequently show a lower toxicity for warm-blooded animals than do the corresponding ethyl ester derivatives. Thus, O,O-dimethyl-p-nitrophenylthiophosphate (metaphos) is less toxic than thiophos [2].

Metasystox-O,O-dimethyl-β-ethylmercaptoethylthiophosphate and its thiol isomer, recently reported by Schrader, are respectively less toxic than systox and Isosystox [3]. Incidentally, it should be mentioned that frequently the methyl esters also show a lower insecticidal activity.

We synthesized the methyl analogs of M-74, being derivatives that contained either methoxyl groups on the phosphorus or methyl groups on the sulfide sulfur, and in this way obtained all four possible combinations.



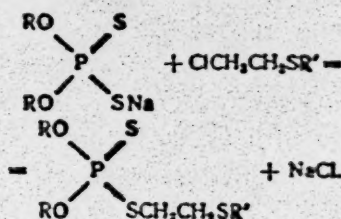
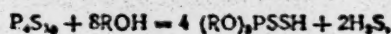
M-74 $\text{R} = \text{R}' = \text{C}_2\text{H}_5$

M-80 $\text{R} = \text{C}_2\text{H}_5$; $\text{R}' = \text{CH}_3$

M-81 $\text{R} = \text{CH}_3$; $\text{R}' = \text{C}_2\text{H}_5$

M-82 $\text{R} = \text{R}' = \text{CH}_3$

These compounds were easily synthesized by the method used by us to obtain M-74 [1]. Specifically, the reaction of phosphorus pentasulfide with either ethyl or methyl alcohol gave us the O,O-dialkylidithiophosphate, which was converted to the sodium salt; the latter was alkylated with either β -chloroethyl methyl or β -chloroethyl ethyl sulfide:



The properties of the obtained compounds and their analysis results are given in Table 1. In addition, we synthesized and studied the properties of the propyl analog of M-74, containing the propyl group on the sulfide sulfur.

As we had expected, the substances that contained methyl groups proved to be less toxic than M-74 for warm-blooded animals, as can be seen from the data in Table 2. The propyl analog proved to be more toxic.

In the laboratory the compounds M-80, M-81, M-82 and M-85 were tested as both contact and systemic insecticides. The contact action of the compounds was determined by spraying them on the last instar larvae of the mealy bug (*Pseudococcus maritimus* Ehrh.) and by immersing the harmful harlequin bug (*Eurygaster integriceps* Put.) in their solutions with an exposure time of 5 seconds. The relative toxicity of the compounds was determined by the concentrations of the active principle in the solutions producing a 95-100% kill of the insects in 7 days. The solutions were prepared from concentrates that contained 30% of the active principle and 70% of synergistic compound OP-7.

The systemic action of the compounds was studied on the harmful harlequin bug by the method of seed-treatment before planting. The spring wheat seed was soaked in a 0.6% solution of the compound being tested, then air-dried, and after a day planted in pots. In 7-10 days after treating the seed the bugs were placed on the wheat sprouts, where they fed on the plant juices. The experimental results were based on the percent mortality of the bugs after being on the plants for 7 days.

The data of the laboratory experiments on the contact and systemic action shown by the above compounds are summarized in Table 3.

In addition, an experiment was run under greenhouse conditions to study the systemic action shown by some of the indicated compounds on the spider mite (*Tetranychus* sp.) found on ornamental plants. The compounds M-74, M-82 and mercaptophos (at an active principle concentration of 0.025%) proved to be very close to each other in their activity toward this pest. Thus, when counted on the 15th day after treatment the reduction in the number of mites was respectively 99.2, 97.7 and 96.7% of the starting amount. Compound M-80 was slightly inferior to the preceding compounds (the reduction in the number of mites was 93.2% in the same length of time).

TABLE 1

Code No.	Formula	B.p., in °C	Pres- sure (mm Hg)	20 n _D	d ₄ ²⁰	C, %		H, %		P, %		S, %	
						found	calc.	found	calc.	found	calc.	found	calc.
M-80	(C ₁₂ H ₁₀ O) ₂ PSSCH ₂ CH ₂ SC ₂ H ₅	155-156	3	1.5405	1.1009	32.19	32.07	0.50	0.47	11.80	11.65	—	—
M-81	(CH ₃ O) ₂ PSSCH ₂ CH ₂ SC ₂ H ₅	91-92	0.003	1.5479	1.2005	20.07	20.25	0.04	0.11	12.40	12.30	38.88	39.03
M-82	(CH ₃ O) ₂ PSSCH ₂ CH ₂ SC ₂ H ₅	71-71.5	0.004	1.5560	1.2403	25.03	25.62	5.65	5.76	13.45	13.46	—	—
M-85	(C ₁₂ H ₁₀ O) ₂ PSSCH ₂ CH ₂ SC ₂ H ₅	143-144	2	1.5275	1.1200	37.31	37.22	7.50	7.28	10.67	10.58	33.15	33.32

It follows from the above data that in its contact action M-74 is most toxic and M-85 is least toxic. With respect to the harlequin bug the compounds M-82 M-81 also showed high insecticidal properties. In their systemic action the compounds M-74, M-82 and M-81 proved to be the most active, and here compound M-85 showed low toxicity.

TABLE 2

Compound	Intravenous toxicity LD ₁₀₀ for rabbits in mg/kg
M-74	3-3.5
M-80	5-5.5
M-81	20
M-82	22-25
M-85	5
Thiophos	7.5

When the insecticidal activity of the above compounds is compared with their toxicity when injected intravenously into rabbits, attention is drawn to the sharp difference in the action of the propyl analog of M-74 (compound M-85). This compound, showing essentially the same toxicity for rabbits as M-74 and M-80, at the same time shows the least insecticidal activity, while compounds M-81 and M-82, being least toxic for warm-blooded animals, in their systemic action toward the harlequin bug and spider mite lie close to M-74. In their contact action they are noticeably inferior to M-74 on harlequin bugs and to a lesser degree on mealy bugs.

TABLE 3

Compound	Solution concentration (in %), producing 95-100% kill by contact action		Mortality of harlequin bugs (in %) after 7 days exposure to the systemic action of 0.6% solutions
	mealy bugs	harmful harlequin bugs	
M-74	0.005	0.0005	85.0
M-80	0.01	0.005	80.0
M-81	0.025	0.0005	82.5
M-82	0.015	0.0005	87.5
M-85	0.05	0.05	25.0
Thiophos	>0.025	0.005	—
Mercaptophos	—	—	60.0

The obtained results are evidence that some M-74 analogs, being less toxic than M-74 for warm-blooded

animals, at the same time are characterized by high insecticidal and acaricidal activity, which is a very important consideration when these compounds are used to protect plants from harmful organisms.

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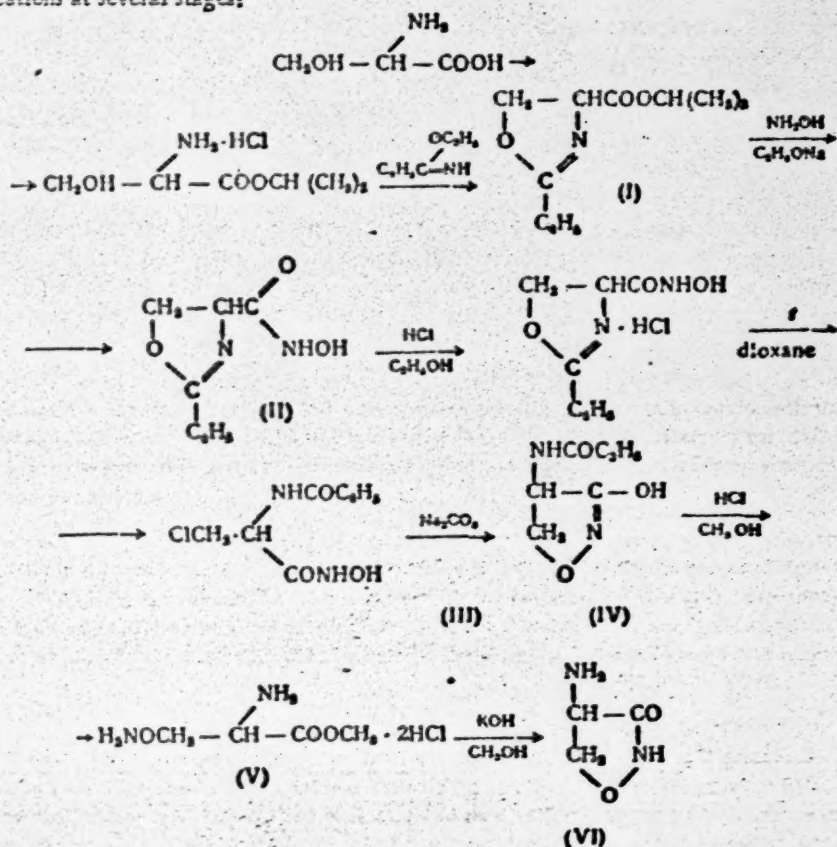
SYNTHESIS OF CYCLOSERINE

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Presented by Academician A. N. Nesmeyanov, March 9, 1958

Recently a communication appeared [1] on the isolation of an antibiotic that was produced by a new strain of *Streptomyces*. It was shown that the new antibiotic, called cycloserine [1], oxamycin [2] or PA-94 [3], shows a broad antibacterial spectrum and high activity in relation to pulmonary tuberculosis and certain infections of the urological tract [4]. At the same time a short communication was published, containing a scheme for the synthesis of cycloserine, without giving experimental details [5].

Taking the proposed scheme as a base, we developed the synthesis of cyclosporine in detail, making substantial modifications at several stages:



When an attempt was made to duplicate exactly the indicated synthesis path for cycloserine we ran into considerable difficulties right at the start, since the 2-phenyl-4-carbomethoxy- Δ^2 -oxazoline, which was the primary starting material, is obtained from d,l-serine methyl ester hydrochloride and the ethyl iminobenzoate in low yield. Consequently, as starting material we used the isopropyl ester of 2-phenyl-4-carboxy- Δ^2 -oxazoline

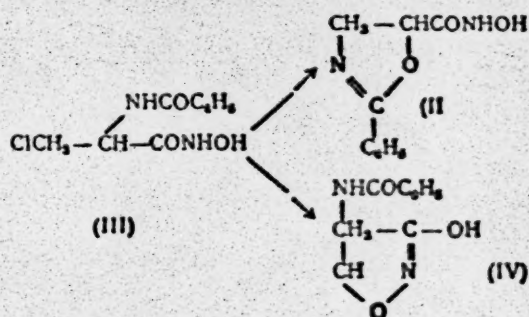
(I), the yield of which reaches 80-82% when the serine isopropyl ester hydrochloride is condensed with ethyl iminobenzoate [6].

When hydroxamic acid (II) was prepared in the usual manner from ester (I), i.e., by reacting (I) with hydroxylamine hydrochloride in the presence of sodium ethylate, it was obtained in moderate yield (40-60%). Considerably better results were obtained if the crystalline hydroxylamine base was used. We ran the synthesis by this method and obtained (II) in better than 80% yield.

An important operation in the synthesis proved to be the transition from hydroxamic acid (II) to the hydroxamic acid of N-benzoyl- β -chloroalanine (III).

It was found that success is obtained if a strictly equivalent amount of hydrogen chloride in dioxane is used. An excess of hydrogen chloride leads to strong tarring, and (III) is obtained in small yield; on the other hand, a deficiency of hydrogen chloride gives a difficultly separable mixture of (II) and (III).

We postulated that the transformation of (II) into (III) goes through the intermediate formation of the hydrochloride which then undergoes thermal isomerization (see [7]). Actually, when (II) is reacted with an alcoholic solution of hydrogen chloride in the cold the hydrochloride is obtained in quantitative yield, which when heated in dry dioxane is isomerized to the benzoylchloroalanine hydroxamic acid (III). Prior to running the isomerization it is essential to remove all traces of hydrogen chloride from the (II) hydrochloride. When this is done the yield of (III) reaches 80-85%, and our modification of this step in the process is of great importance. The cyclization of hydroxamic acid (III) can proceed in two directions, leading either to the 4-benzamidoxazolidone (IV) or back to the hydroxamic acid (II).



The transformation of (III) into (IV) when treated with 1N potassium hydroxide solution, as was indicated in the communication on the synthesis of cycloserine [5], fails to give satisfactory results. Here the hydroxamic acid (III) is always formed in predominant amount (60%), while the desired reaction product (IV) is formed in a total yield of only 20%.

When a 20% aqueous soda solution was used as the cyclization agent, we were able to achieve the desired reaction direction and obtained the benzoyl derivative in 70% yield. Under our conditions there is some parallel formation of (II), which, however, doesn't interfere with the isolation of pure (IV). Treatment of benzoyl derivative (IV) with hydrogen chloride in absolute methanol solution gave the dihydrochloride of the α -aminohydroxyalanine derivative, which when treated with 1N alcoholic caustic solution was converted into racemic cycloserine.

EXPERIMENTAL

2-Phenyl-4-carbohydroxamido- Δ^2 -oxazoline. To a solution of 48 g of 2-phenyl-4-carbisopropoxy- Δ^2 -oxazoline in 140 ml of absolute alcohol was added 11 g of crystalline hydroxylamine base. The reaction mixture was stirred until the hydroxylamine had dissolved and then with stirring and ice-water cooling an alcohol solution of sodium ethylate (4.8 g of sodium in 75 ml of absolute alcohol) was added dropwise. When all of the alcoholate had been added the reaction mixture was stirred at room temperature for 15-20 minutes, and then under cooling was neutralized with 10% hydrochloric acid until neutral to bromthymol blue. The resulting precipitate was filtered, washed with water, alcohol and ether, and then air-dried. The yield of 2-phenyl-4-carbohydroxamido- Δ^2 -oxazoline was 38.0 g (92%), m.p. 172-174°. After recrystallization from water the substance melts at 175-177°.

Found %: C 58.84; H 5.06; N 13.40, 13.31. $C_{10}H_{10}O_2N_2$. Calculated %: C 58.20; H 4.88; N 13.60.

2-Phenyl-4-carbohydroxamido- Δ^2 -oxazoline is a white crystalline substance, giving a cherry-red color with aqueous $FeCl_3$ solution. Difficultly soluble in the ordinary organic solvents. It can be recrystallized from dioxane, water and aqueous alcohol.

2-Phenyl-4-carbohydroxamido- Δ^2 -oxazoline Hydrochloride. To a suspension of 10 g of 2-phenyl-4-carbohydroxamido- Δ^2 -oxazoline in 20-30 ml of absolute alcohol was added with stirring and cooling 10 ml of a 25% alcoholic solution of hydrogen chloride; here the substance went into solution immediately and then the hydrochloride of 2-phenyl-4-carbohydroxamido- Δ^2 -oxazoline began to crystallize, and was filtered and washed first with absolute alcohol and then with ether. M.p. 114-116°. The yield was quantitative.

Found %: Cl 14.61, 14.54. $C_{10}H_{11}N_2O_2Cl$. Calculated %: Cl 14.61.

d,l- α -Benzamido- β -chloropropionohydroxamic Acid (III). Five grams of 2-phenyl-4-carbohydroxamido- Δ^2 -oxazoline hydrochloride was suspended in 15-20 ml of absolute dioxane and heated with stirring until dissolved. The hot solution was filtered, cooled, the resulting precipitate filtered, washed with a small amount of absolute alcohol, and then with ether. The yield of d,l- α -benzamido- β -chloropropionohydroxamic acid was 4.2 g (84%), m.p. 147-149°. After recrystallization from a mixture of alcohol and ethyl acetate, m.p. 153-155°.

Found %: C 49.25, 49.50; H 4.65, 4.68; N 11.11, 11.16; Cl 14.20, 14.38. $C_{10}H_{11}O_3N_2Cl$. Calculated %: C 49.40; H 4.56; N 11.54; Cl 14.61.

Colorless crystalline substance with relatively low solubility in the ordinary organic solvents and water.

d,l-4-Benzamido-3-isoxazolidone (IV). d,l- α -Benzamido- β -chloropropionohydroxamic acid (14.8 g) was dissolved in 40 ml of 20% aqueous soda solution with heating. The reaction mixture was boiled for 1-2 minutes, then cooled, and neutralized with 20% acetic acid until neutral to bromthymol blue. The resulting precipitate of (II) was filtered, and weighed 2.2 g (17.6%), m.p. 168-172°. The mixed melting point with authentic 2-phenylcarbohydroxamido- Δ^2 -oxazoline was not depressed, m.p. 169-171°. The substance gives a cherry-red color with aqueous $FeCl_3$ solution and when treated with methanolic hydrogen chloride solution it gives the hydrochloride with m.p. 110-112°. The mixed melting point with the authentic hydrochloride of (II) was not depressed. The filtrate was acidified with dilute acetic acid until it showed acid to bromthymol blue. The resulting precipitate of (IV) was filtered and dried in a vacuum-desiccator over P_2O_5 . The yield of d,l-4-benzamido-3-isoxazolidone was 10.0 g, m.p. 155-157°. Recrystallization from water gave 8.8 g (70%) of substance with m.p. 164-166°.

Found %: C 57.71, 57.81; H 4.82, 4.91; N 13.48, 13.39. $C_{10}H_{10}O_3N_2$. Calculated %: C 58.24; H 4.89; N 13.59.

Colorless crystalline substance, difficultly soluble in the ordinary organic solvents; it fails to give a coloration with aqueous ferric chloride solution.

d,l- β -Aminohydroxyalanine Methyl Ester Dihydrochloride (V). To 4.0 g of d,l-4-benzamido-3-isoxazolidone was added 30 ml of a 35% methanolic solution of hydrogen chloride. The reaction mass was heated on the water bath for 1.5-2 hours, filtered, and ether added to the filtrate. The resulting oil crystallized when rubbed with ether. The product was recrystallized from absolute alcohol. The yield of d,l- β -aminohydroxyalanine methyl ester dihydrochloride was 2.8 g (70%), m.p. 146-148°.

Found %: C 22.53, 22.56; H 5.78, 5.81; Cl 33.91, 33.79. $C_{11}H_{12}O_3N_2Cl_2$. Calculated %: C 23.20; H 5.85; Cl 34.24.

d,l-4-Amino-3-isoxazolidone (Racemic Cycloserine). Dihydrochloride (V) (0.3 g) was added to 4.1 ml of alcoholic KOH solution (containing 0.036 g KOH in 1 ml), the potassium chloride was quickly filtered, the alcohol solution was evaporated *in vacuo* to 1/2 volume, 1-2 ml of ether was added, the resulting precipitate was filtered, and then recrystallized from aqueous alcohol. Yield 0.3 g (66%), m.p. 132-134° (with decomp.).

Found %: C 35.52, 35.55; H 6.09, 5.99; N 27.54, 27.57. $C_5H_8O_2N_2$. Calculated %: C 35.29; H 5.92; N 27.45.

Colorless crystalline substance, readily soluble in water and difficultly soluble in organic solvents. Crystallizes from aqueous alcohol as colorless needles.

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THE STRUCTURE OF THE EQUILIBRIUM DIAGRAMS OF MULTICOMPONENT HETEROGENEOUS SYSTEMS

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Presented by Academician I. I. Chernyaev, March 22, 1958

To develop further the topological analysis of the equilibrium diagrams of multicomponent heterogeneous systems, the foundation of which was laid by the studies of N. S. Kurnakov [1], and to study the general topological structure of the indicated diagrams, it is possible to make use of the rule of contacting regions of separation [2,3]:

$$R_1 = R - D^- - D^+ \geq 0, \quad (1)$$

where R is the DE dimension (for DE of n -component systems $R = n + 1$), R_1 is the dimension of the boundary between two adjacent RS's and D^- and D^+ are respectively the number of vanishing phases and the number of newly arisen phases in the passage of the figurative point from one RS to another across a given boundary. In using RCRS and DE it is necessary first to eliminate degeneration of the corresponding RS's [3].

Each DE represents an R -dimensional screen, composed of the boundaries (certain hypersurfaces in the R -dimensional space of the DE) between RS's. The RS's are the R -dimensional meshes of this screen. The maximum dimension of the boundary between two RS's is evidently equal to $R-1$. Intersecting among themselves, the $R-1$ -dimensional hypersurfaces of DE form a series of nodes**--geometric elements of smaller dimensions: from $R-2$ to zero (point) inclusive, which also serve as boundaries between corresponding RS's in the DE. In order that RCRS can be used to study the topological structure of DE we will develop a structure for the above-indicated R -dimensional screen in DE and such an arrangement of phases along RS as will satisfy RCRS.

First of all we will examine the area around the zero-dimensional node (point) in the R -dimensional screen of DE. It can easily be shown that the structure of the area around the given point should be topologically equivalent to $R-1$ -dimensional hypersurfaces intersecting R times among themselves. Actually, only for the indicated topological structure is it possible to distribute the phases along the boundary through a given point RS in such manner that RCRS is satisfied. From this it is easy to determine the number of geometric elements of different dimensions emanating from the indicated point, and also to find the rule of phase grouping (RGP), which is obeyed by the phase distribution along RS. In like manner it is immediately possible to generalize the obtained results for the case of an m -dimensional node in DE. For this we will mention that RCRS (1) embraces not only DE, but also the regular (non-nodal [3]) sections of DE. In the latter case R in formula (1) is equal to the dimension of the regular section in DE and is different from $n + 1$. Here we form R —an m -dimensional regular section of DE, in which the vestige of the original m -dimensional node in DE will be represented by a point. Since from the previous RCRS (1) is valid for the given DE section, the area around the mentioned point, according to the above, should represent a figure that is topologically equivalent to $R - m - 1$ -dimensional hyperplanes intersecting $R - m$ times.

In the reverse transition from an $R - m$ -dimensional regular section to an R -dimensional DE all of the geometric elements of the indicated figure acquire additional m dimensions: the central point of the figure is again transformed into the m -dimensional node of DE, the lines emanating from the central point are transformed into $m + 1$ -dimensional hypersurfaces, etc., and the $R - m$ -dimensional RS's become R -dimensional. Consequently, subsequently we will use the following abbreviations: DE) equilibrium diagram, RS) region of separation, RCRS) rule of contacting regions of separation, and RGP) rule of grouping of phases.

** In the general case we call the intersection of a certain number of hypersurfaces a node.

we arrive at the result that the area around an m -dimensional node in an R -dimensional DE is topologically equivalent to $R-1$ -dimensional hypersurfaces intersecting $R-m$ times among themselves. In accord with this the following formula holds:

$$X_l^m = 2^{l-m} C_{R-m}^{l-m}, \quad 0 \leq m \leq R-1, \quad m \leq l \leq R. \quad (2)$$

where C_{R-m}^{l-m} is the number of combinations from $R-m$ along $l-m$, and X_l^m represents the number of elements of the l -th dimension, emanating from our examined DE m -dimensional node. In accord with Formula (2), for $l=m$ we have $X_m^m = 1$, which corresponds to the central m -dimensional node of the given figure; for $l=R$ we have $X_R^m = 2^{R-m}$, which gives the number of R -dimensional elements in the examined figure, i.e. the number of RS's that pass as bordering pairs through the indicated m -dimensional node.

Consequently, we can ascertain to what extent the geometrical elements of different dimensions correspond to each of these RS's. Evidently, here the formula holds:

$$u_l^m = C_{R-m}^{l-m}, \quad 0 \leq m \leq R-1, \quad m \leq l \leq R, \quad (3)$$

where u_l^m is the number of l -dimensional elements belonging to one RS in the examined figure.

In a similar manner the rule for the grouping of phases RGP along RS's passing as bordering surfaces through a zero-dimensional node (through a point), is made general on the case of an m -dimensional node in the DE. For an m -dimensional node RGP has the following character.

First of all, among the RS's passing as bordering surfaces through a given m -dimensional node in the DE, there exists $C_{R-m}^0 = 1$ — one RS with a minimum number of phases (for example, λ phases). The phases entering into the composition of this RS (for example, the phases: $\alpha_1, \alpha_2, \dots, \alpha_\lambda$), also enter into the composition of all of the other indicated RS's. Among these RS's there also exists $C_{R-m}^{R-m} = 1$ — one RS with a greater number of phases, equal to $\lambda + R-m$ (into its composition enter the phases: $\alpha_1, \dots, \alpha_\lambda, \alpha_{\lambda+1}, \dots, \alpha_{\lambda+R-m}$). In the composition of the remaining RS's are included the indicated phases: $\alpha_1, \alpha_2, \dots, \alpha_\lambda$ (we will call the combination of these phases: $\alpha_1 + \alpha_2 + \dots + \alpha_\lambda$ the nucleus for the examined RS's), and in addition, various combinations of the phases $\alpha_{\lambda+1}, \alpha_{\lambda+2}, \dots, \alpha_{\lambda+R-m}$ along $R-m-1$, along $R-m-2$, etc. to the combinations along one phase inclusively. That is, we have $C_{R-m}^{R-m-1} = R-m$ RS's with compositions, representing the indicated nucleus plus various combinations of $R-m$ phases $\alpha_{\lambda+1}, \alpha_{\lambda+2}, \dots, \alpha_{\lambda+R-m}$ along the $R-m-1$ phase; we have C_{R-m}^{R-m-2} RS's with compositions, representing the indicated nucleus plus various combinations of the phases $\alpha_{\lambda+1}, \alpha_{\lambda+2}, \dots, \alpha_{\lambda+R-m}$ along the $R-m-2$ phases, etc. . . . ; we have C_{R-m}^1 RS's with compositions, representing the indicated nucleus plus various combinations of the phases $\alpha_{\lambda+1}, \alpha_{\lambda+2}, \dots, \alpha_{\lambda+R-m}$ along two phases; and finally, we have $C_{R-m}^0 = R-m$ RS's with compositions, representing the indicated nucleus plus various combinations of the phases $\alpha_{\lambda+1}, \alpha_{\lambda+2}, \dots, \alpha_{\lambda+R-m}$ along one of these phases. The total number of all of these RS's, passing as bordering surfaces through the mentioned m -dimensional node in the DE, is equal to $C_{R-m}^0 + C_{R-m}^1 + \dots + C_{R-m}^{R-m-1} + C_{R-m}^{R-m} = 2^{R-m} = X_R^m$ in accord with formula (2).

The results obtained above, reflecting the structure of R -dimensional DE's and RGB's, can also be extended to the case of R -dimensional regular (non-nodal) sections in DE's, for which, as was indicated above, formula (1) also holds.

For two-dimensional DE's and two-dimensional regular (non-nodal) sections in DE's ($R=2$) the general considerations discussed above lead to the following results. Only $2^{2-m} = 2^{2-1} = 2$ — two RS's (see Fig. 1, a), the compositions of which (for example, $\alpha_1 + \alpha_2 + \dots + \alpha_\lambda$ and $\alpha_1 + \alpha_2 + \dots + \alpha_\lambda + \alpha_{\lambda+1}$) fail to differ by more than one phase, can border across one line ($m=1$). As a result, one of these RS's ($C_{2-1}^0 = C_1^0 = 1$) possesses a minimum number of phases — λ , and the other of these two RS's ($C_{2-1}^{2-1} = C_1^1 = 1$; $C_1^0 + C_1^1 = 2$) possesses a maximum

number of phases equal to $\lambda + R - m = \lambda + 1$. In two-dimensional DE's or in the two-dimensional regular sections found in DE's only $2^{R-m} = 2^2 = 4$ RS's can border in pairs through one point ($m = 0$) (see Fig. 1.b). The distribution of the phases along the indicated RS's proceeds in accord with RGB as indicated below. Here we have one ($C_{R-m}^R = C_2^2 = 1$) RS with a minimum number of phases (for example, λ phases: $\alpha_1, \alpha_2, \dots, \alpha_\lambda$). The composition of this RS serves as the nucleus for all of the other RS's in the given figure (Fig. 1b). We also have one ($C_{R-m}^R = C_2^2 = 1$) RS with a maximum number of phases, equal to $\lambda + R - m = \lambda + 2$ (for example, phases $\alpha_1, \dots, \alpha_\lambda + \alpha_{\lambda+1}, \alpha_{\lambda+2}$). And finally, we have two ($C_{R-m}^R = C_{R-m}^{R-1} = C_2^1 = 2$) RS's with compositions ($\alpha_1 + \dots + \alpha_\lambda + \alpha_{\lambda+1}$, and $\alpha_1 + \dots + \alpha_\lambda + \alpha_{\lambda+2}$) representing the indicated nucleus plus various combinations of two phases $\alpha_{\lambda+1}$ and $\alpha_{\lambda+2}$ along one phase. It can easily be seen from an examination of Fig. 1b that the area around the zero-dimensional node (point) in either a two-dimensional DE or in a two-dimensional regular section of the DE is topologically equivalent to two ($R-2$) showing mutual intersection by a one-dimensional ($R-1=1$) line, i.e. four lines emanate from each node of this nature. As a result, either a two-dimensional DE or a two-dimensional regular section in a DE topologically represents a two-dimensional screen, each zero-dimensional node of which serves as the origin of four lines.*

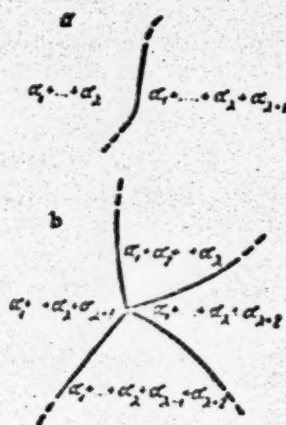


Fig. 1

nucleus L plus various combinations of phases A, B and C along two phases. Here it is also not difficult to see that the area around the eutectic point is topologically equivalent to three ($R = 3$) showing mutual intersection by two-dimensional ($R-1 = 2$) planes.

Any system with an arbitrary number of components can be examined and described in a similar manner.

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*We will mention that in order to develop the indicated structure of two-dimensional DE's or of two-dimensional regular sections in DE's it is necessary to first eliminate degeneration of the corresponding RS's [3].

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THE FORMATION OF BENZENE HOMOLOGS AND THE SPECIFIC ROLE OF THE SURFACE IN THE THERMAL-CATALYTIC TRANSFORMATIONS OF ISO-BUTYLENE IN THE PRESENCE OF BORON FLUORIDE

Ya. M. Paushkin and A. G. Khilzenrat

Presented by Academician A. V. Topchilev, December 28, 1955

In contrast to previous investigations [1-3], in the present study the transformation of butylene was studied. In the temperature interval from 100° to 500° in the presence of boron fluoride gas on such carriers as activated charcoal, aluminum oxide, aluminosilicate and silica gel, and the promoting role of the boron fluoride carrier was shown, on the basis of which it is possible to make a number of interesting conclusions relative to the theory of acidic catalysis.

The polymerization was run on porous carriers, saturated with boron fluoride. The carriers are characterized in Table 1. At 100° the activated charcoal adsorbs a greater amount of BF_3 than do the oxides, and at 400° it adsorbs a smaller amount, in which connection a part of the boron fluoride on the oxides is adsorbed irreversibly, and consequently is chemically bound [4]. Boron fluoride is desorbed by activated charcoal when the temperature is raised.

The polymerization was run in a flow reactor, which was a cylindrical glass tube with external electrical heating. A thermocouple placed in a glass well inside the reactor was used to measure the temperature of the reaction zone. At a reaction temperature of 200-500° an important factor is the isolation of the high-temperature reaction zone from the low-temperature zone, since otherwise a part of the BF_3 can be carried out with the gas stream into the low-temperature zone and receiver, forming catalytic centers here, as a result of which polymerization can take place at temperatures lower than those prevailing in the reactor. We used a special alkaline barrier of granular soda lime, placed in the lower heated portion of the reactor ahead of the receiver, to separate the high-temperature zone from the low-temperature area. Such a barrier trapped all of the BF_3 and it did not enter the low-temperature zone. This feature is novel for the polymerization of olefins with volatile gaseous catalysts in a flow system.

In reaction process the isobutylene was passed through a drying column filled with calcium chloride at a definite rate, controlled with a rheometer, into the reactor, where the boron fluoride gas, obtained by the decomposition of boron fluoride monohydrate with sulfuric acid under heating to 80-100°, was also admitted. The rate of boron fluoride evolution was regulated by the rate with which the monohydrate was added from a calibrated burette. The liquid reaction products were collected in the receiver, while the gaseous products were collected in the gas holder. For the isobutylene transformation products obtained in this manner we determined the density, molecular weight, bromine number, aniline point, and group composition, and we also ran a precise rectification through a column with a fractionation capacity equivalent to 15 theoretical plates.

TABLE 1
Characterization of the Boron Fluoride Carriers

Carrier	Average pore size in Å	Amount of BF_3 adsorbed in wt. % at a temperature of			
		100°	200°	300°	400°
Activated charcoal (BAU)	73.8	14.1	8.8	4.3	0.9
Aluminum oxide Al_2O_3	65.9	13.4	9.2	5.5	3.2
Silica gel SiO_2	45.4	10	7.6	5.8	2.0
Aluminosilicate $\text{Al}_2\text{O}_3 \cdot n\text{SiO}_2 \cdot m\text{H}_2\text{O}$	45.0	9.3	7.1	7.0	2.3

TABLE 2

Transformation of Isobutylene in the Presence of BF_3 on Various Carriers at 400°

Carrier	Conversion %	d_4^{20}	n_D^{20}	M.W.	Bromine number	Product composition in %	
						olefins	others
No transformation obtained							
Activated charcoal + BF_3	14	0.7315	1.4290	138	88	75	25
$\text{SiO}_2 + \text{BF}_3$	43	0.7225	1.4134	98	106.8	63	37
$\text{Al}_2\text{O}_3 + \text{BF}_3$	20	0.7248	1.4200	121	88	64	36
$\text{Al}_2\text{O}_3 + \text{SiO}_2 + \text{BF}_3$							

TABLE 3

Transformation of Isobutylene at High Temperatures and Atmospheric Pressure in the Presence of Boron Fluoride on Aluminum Oxide

Temp. in °C	Amount of converted isobutylene in the liquid product in %	d_4^{20}	n_D^{20}	Mol. wt.	Bromine number	Aniline point *	Group composition in %		
							Olefins	Paraffins	Aromatic
165	92	0.7552	1.4344	168	89.4	—	95	5	—
300	84	0.7316	1.4220	115	105.8	+12	78	24	—
400	43	0.7225	1.4134	99	105.8	+38	65	30	—
500	28	0.8142	1.4849	104	48.1	-15	32	43	—

* Temperature of dissolving in aniline.

The carrier in the reactor, the amount of which prior to experiment was 80 ml, was vacuum-dried at 200° and then saturated with BF_3 at the experimental temperature. The polymerization process was run at a space velocity of 60-65 hour⁻¹; 100 liters of isobutylene was used per experiment. True isobutylene polymerization is the main reaction at an experimental temperature of 200°. However, in the presence of BF_3 on oxide catalysts about 15-20% of saturated products is formed. At 400°, as can be seen from Table 2, neither polymerization nor other isobutylene transformations take place in the presence of boron fluoride on charcoal, but in the presence of metal oxides and boron fluoride both polymerization and other transformations are observed. The reaction products consist of olefins and saturated hydrocarbons, which are obtained as the result of hydrodehydrodimerization and other transformations. Consequently, oxide carriers and especially aluminum oxide promote the isomerization of isobutylene in the presence of boron fluoride.

The character of the obtained isobutylene polymers also varies as a function of the carrier used in the polymerization. On charcoal with BF_3 at 200° the polymers contain a greater amount of olefins than when the oxide catalysts with BF_3 are used (98% versus 80-85%). At 400° in the presence of BF_3 and charcoal the transformation of isobutylene is completely absent while with BF_3 on aluminum oxide the conversion reaches 43% which apparently is associated with the formation of surface-active structures between the BF_3 and Al_2O_3 , and also with other oxides. The fact that a part of the BF_3 on oxides is irreversibly adsorbed speaks in favor of this postulation.

The influence of temperature on the experimental results is very easily seen from the data in Table 3. At 500° and atmospheric pressure the isobutylene transformation proceeds with the formation of 70% of aromatic and naphthenic hydrocarbons.

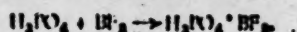
The individual hydrocarbons were identified by means of Raman spectra (Table 5). * The aromatic transformation products of isobutylene at 500° show concentration in the fractions 120-150°, 150-170°, and higher. These fractions consist almost completely of aromatic hydrocarbons. It is interesting to mention that the reaction

TABLE 4

Characterization of the Fractions of Isobutylene Transformation Products on Catalyst $\text{BF}_3 + \text{Al}_2\text{O}_3$ at 500°

Boiling range of the fraction in °C	Yield in %	d_4^{20}	n_D^{20}	Mol. wt.	Bromine number	Unsaturates in %	Aromatic	Aniline point
27-100	18	0.7055	1.3935	91	102.0	88	—	+38
100-120	9.0	0.7449	1.4296	102	23.0	15	—	+25
120-150	17.0	0.8375	1.4765	113	4.2	3	74	-16
150-170	25.0	0.8433	1.4845	117	0.8	3	85	—
170-203	13.5	0.8679	1.5006	—	—	—	—	—
residue >203	17.5	0.920	1.5930	—	—	—	—	—

* The hydrocarbon composition was determined with the kind cooperation of Prof. G. M. Panchenkova.



Charcoal, made anhydrous at high temperatures of 300-500°, is incapable of forming catalytically active structures with boron fluoride, and consequently activated charcoal fails to promote catalysis in the presence of

TABLE 5

Individual Hydrocarbons in the Catalytic Transformation Products of Isobutylene on Catalyst $\text{BF}_3 + \text{Al}_2\text{O}_3$

Experimental temperature in °C	Boiling range of fraction in °C	Hydrocarbons	B. p. of the hydrocarbon in °C
100	100-110	2,4,4-trimethyl-1-pentene	101.4
		2,4,4-trimethyl-2-pentene	104.9
300	110-120	2,3,4-trimethyl-1-pentene	117.3
400		2,3,4-trimethyl-2-pentene	119.3
500	120-140	p-xylene 20%	144.4
		m-xylene 60%	129.1
		p-xylene 20%	134.3
500	150-170	1,2,4-trimethylbenzene (mesitylene)*	164.7
		1,2,4-trimethylbenzene (pseudocumene) 45%	169
		1,2,3-trimethylbenzene 25%	178

TABLE 6

Calculated and Experimental Data on Isobutylene Conversion in the Transformation Products

Temperature, °C	ΔT°	K_p°	Equilibrium yield of dimer, %	Yield of liquid product based on isobutylene, %
100	-4937	+4.044	99	92-98
200	-2498	+1.247	84-91	84
300	+1537	-0.544	20-28	54
400	+5773	-1.873	3-4	43
400	+16013	-2.831	1-3	39

* For 2,4,4-trimethyl-1-pentene.

** For 2,4,4-trimethyl-1 and -2-pentenes.

BF_3 . As a result, the mechanism of the promoting action shown by adsorbent surfaces on the catalytic activity of boron fluoride at elevated temperatures reduces to the formation of catalytically active structures of acidic type, i.e., to acidic catalysis. At low temperatures the water adsorbed on the carrier surface gives catalytically active acidic structures of the type of $\text{H}^+(\text{HO}\cdot\text{BF}_3)^-$ with boron fluoride. These boron fluoride hydrates are easily decomposed at elevated temperatures.

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EQUILIBRIUM PHASE DIAGRAMS OF THE SYSTEMS $\text{NaCl-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{CaSO}_4\text{-H}_2\text{O}$ and $\text{SiO}_2\text{ (Quartz)-H}_2\text{O}$

Corresponding Member Acad. Sci. USSR M. A. Styrikovich and I. Kh. Khaibullin

The physicochemistry of vapor solutions is now in the initial stages of development and requires both experimental and theoretical study.

At high pressures steam acquires the ability to dissolve various nonvolatile substances, which to a large degree determines the contamination of steam by the impurities found in boiler water, and also their deposition in turbines.

In the Energetics Institute of the Academy of Sciences of the USSR a study was made of the rules governing the solubility of a number of nonvolatile substances in steam at high and ultrahigh pressures. The data thus obtained permitted constructing the equilibrium phase diagrams of the systems $\text{NaCl-H}_2\text{O}$, $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$, $\text{CaSO}_4\text{-H}_2\text{O}$ and $\text{SiO}_2\text{ (quartz)-H}_2\text{O}$, of great importance in understanding the physicochemical processes that take place inside of boilers. Literature data on the solubility of these compounds in steam and in water [1-11] and on the vapor pressure of their saturated solutions [12-14] were used in the construction of the diagrams.

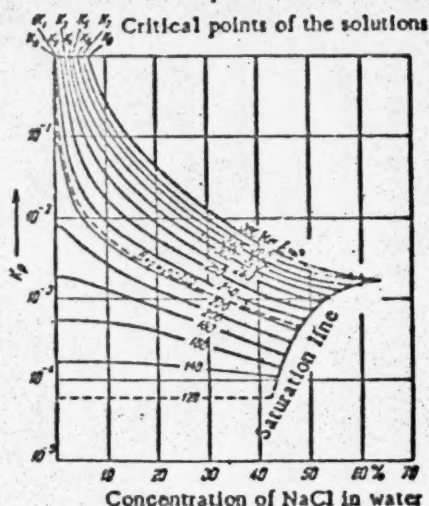


Fig. 1. Plot of the equilibrium phase constant K_e for the system $\text{NaCl-H}_2\text{O}$ as a function of pressure and composition.

The points of intersection of the isobars with the lines of the saturated solutions form the C-P-t diagram of saturated aqueous NaCl solutions.

The represented systems can be regarded as being two-component with volatile (H_2O) and high-melting (salt and quartz) components, i.e., systems in which the ternary point of one component is found at a considerably higher temperature than the critical point of the other component. Consequently, the phase diagrams of these systems should include the regions of liquid (aqueous), vapor and postcritical solutions.

The equilibrium phase diagram of the system $\text{NaCl-H}_2\text{O}$ is shown in Fig. 2. The lower portion of the diagram embraces the region of aqueous sodium chloride solution. It is bounded by a saturated solution line that starts at the freezing point of saturated NaCl solution ($t = -21.1^\circ$, $C = 23.2\%$) and ends in the melting point of the salt ($t = 804^\circ$), where the NaCl concentration in water is 100%; here the isobars, expressing the relationship between the boiling points of the aqueous solutions and the concentration, embrace the pressure range from 1 to 400 kg/cm^2 . The isobars, corresponding to pressures $P \leq P_{\text{H}_2\text{O}}^{\text{cr}}$ originate from the boiling points of pure water, while the isobars, corresponding to pressures $P > P_{\text{H}_2\text{O}}^{\text{cr}}$ begin from the

The region of the vapor and postcritical solutions of the NaCl-H₂O system is shown in the upper portion of the diagram. Here the left portion characterizes the region of the vapor solutions found in equilibrium with the aqueous solutions; and the right portion characterizes the equilibrium region of superheated steam with the solid salt. Geometrically the points corresponding to the boiling points of the saturated solutions on the solubility isobars of NaCl in steam show the saturated vapor solutions of the given system.

The region for the equilibrium of the vapor solutions with the aqueous solutions can be most clearly expressed by the phase equilibrium constant K_e , characterizing the distribution of the dissolved component between

the vapor and liquid phases at a given pressure. The isobars for the phase equilibrium constant of the NaCl-H₂O system are shown in Fig. 1. The composition of the liquid phase (in % NaCl) is plotted along the abscissa, while the phase equilibrium constant is plotted along the ordinate. From the diagram it can be seen that at $P < P_{H_2O}^{cr}$ equilibrium salt solutions exist in both the vapor and liquid phases of the system up to zero concentration for the dissolved component; in this connection the limiting value of the phase equilibrium constant depends only on the pressure and can be calculated from the formula

$$K_e = (\gamma^v / \gamma^l)^n \quad (1)$$

where n for NaCl is equal to 4.4, and γ^v and γ^l are the vapor and water densities, respectively.

At $P > P_{H_2O}^{cr}$ the limiting phase equilibrium constant is equal to unity and corresponds to the critical composition of the system at a given pressure. When $P = P_{H_2O}^{cr}$, $K_e = 1$ at zero concentration for the dissolved component, which compounds to the critical point of water.

At the minimum temperature point the isobars of the vapor solutions (Fig. 2), corresponding to pressures $P > P_{H_2O}^{cr}$, show transition without a break into the corresponding isobars of the liquid (aqueous) solutions in the given system. The combination of these points forms the critical line of the NaCl-H₂O system, which connects the critical point of water (lower critical point in the system) with the critical point of sodium chloride (upper critical point in the system).

The equilibrium phase diagrams of the systems, Na₂SO₄-H₂O, CaSO₄-H₂O and SiO₂ (quartz)-H₂O are shown in Figs. 3 and 4. They resemble each other

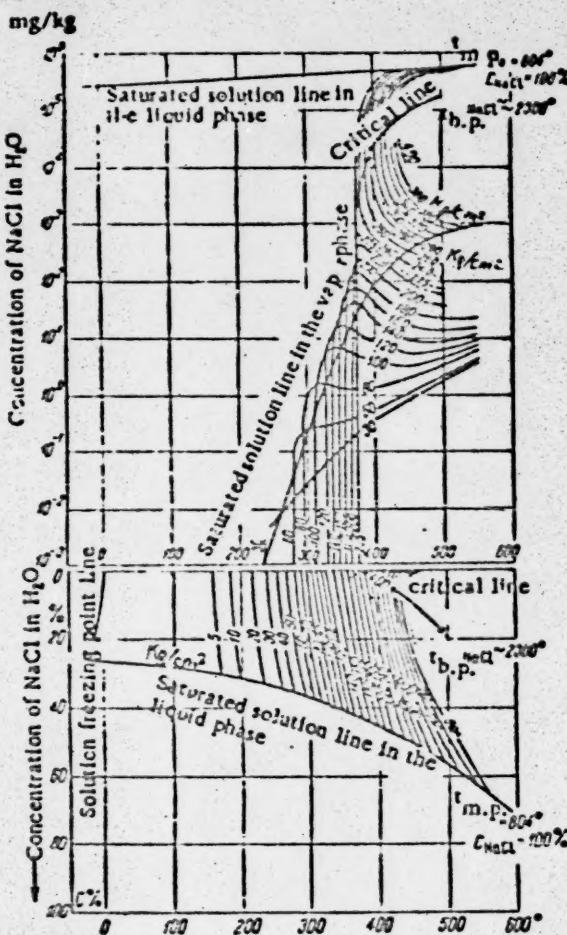


Fig. 2. Equilibrium phase diagram of the system NaCl-H₂O.

and differ strongly from the system NaCl-H₂O. The water solutions of these substances show very little temperature depression and a negative solution heat at elevated temperatures. Consequently, a critical region is absent in these systems, while the critical solution line shrinks into a point, practically identical with the solvent-water critical point. The upper boundary lines represent saturated solutions in the liquid phase of the system, while the lower lines represent saturated solutions in the vapor phase. These lines merge in the critical point. The ratio of the vapor phase concentration to the liquid phase concentration at a constant temperature (pressure) gives the phase equilibrium constant of the system for a given pressure. The latter, as was shown by experiment, for systems that form weak solutions and show a low temperature depression is practically independent of the concentration and can be calculated from equation (1).

• For the sake of clarity the isobars of the aqueous solutions, corresponding to pressures $P > P_{H_2O}^{cr}$ and the saturation line in the liquid phase are reproduced in the upper portion of the diagram.

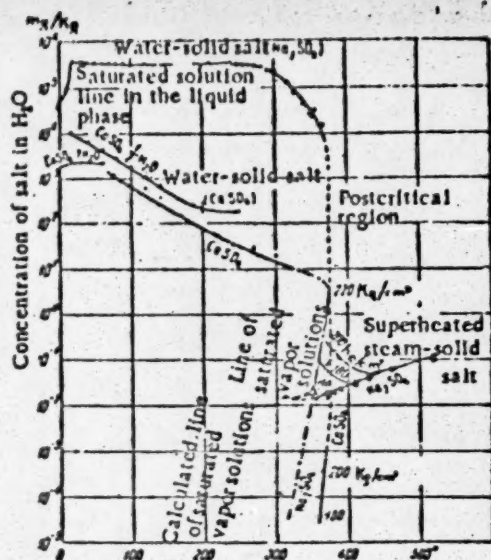


Fig. 3. Equilibrium phase diagram of the systems $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{CaSO}_4\text{-H}_2\text{O}$.

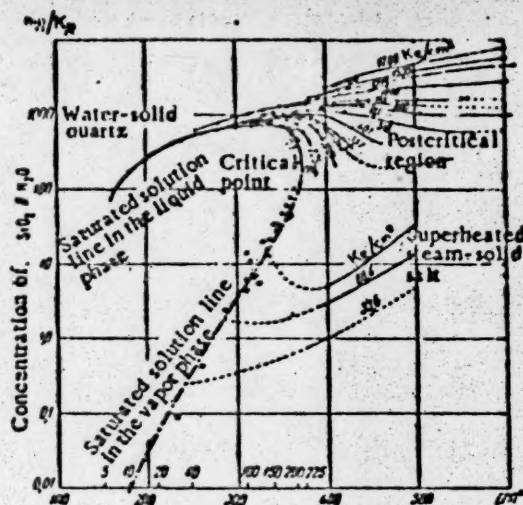


Fig. 4. Equilibrium phase diagram of the system $\text{SiO}_2(\text{quartz})\text{-H}_2\text{O}$.

At pressures below 160 kg/cm^2 ($t = 346^\circ$) the experimental vapor solution saturation line in the system $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ differs from the calculated. This is apparently due to the fact that in the experiments run at $K_e < 10^{-6}$ some vapor entrainment was encountered, which raised the total loss coefficient.* Consequently, on the equilibrium phase diagram of the $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ system (see Fig. 3) the calculated saturation line for sodium sulfate vapor solutions is the more reliable at pressures below 160 kg/cm^2 . The isobars situated to the right of the vapor phase saturation line characterize the solubility of the nonvolatile components of the system in superheated steam.

Data on the solubility of quartz in water at ultrahigh pressures (up to 1780 kg/cm^2) [4] are also plotted on the equilibrium phase diagram of the system $\text{SiO}_2(\text{quartz})\text{-H}_2\text{O}$ (see Fig. 4). They form a family of solubility isobars of SiO_2 in water, being regularly shaped curves of its saturated solutions in both the liquid and vapor phase.

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* The phase equilibrium constants of the systems $\text{Na}_2\text{SO}_4\text{-H}_2\text{O}$ and $\text{CaSO}_4\text{-H}_2\text{O}$ were determined by the method of labeled atoms using S^{35} isotope.

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THE EXTRACTION OF NIOBIUM, TANTALUM AND TITANIUM CUPFERRATES

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A considerable number of papers have been published on the extraction of metal cupferrates with various organic solvents [1-4]. It can be concluded from these studies that most cupferrates are extracted from acid solutions. Data on the extraction of cupferrates from weakly acidic and neutral solutions are practically non-existent.

The extraction of small amounts of niobium cupferrate is discussed in the paper by K. V. Troitsky [5]. The problem of extracting tantalum cupferrate is not discussed in the literature.

Our problem was to make a detailed study of the extraction of niobium and tantalum for the purpose of determining the possibility of their separation from titanium.

Extraction of Niobium Cupferrate. To study the extraction of niobium cupferrate we investigated the solutions of the pyrosulfate melts of niobium pentoxide in 2% ammonium binoxalate, ammonium bitartrate and ammonium bicarbonate, and also in hydrochloric and sulfuric acids. The Nb_2O_5 concentration was 0.6-0.9 mg/ml. The extraction was done as follows. To 5 ml of the studied solution was added 3 ml of a 6% aqueous cupferron solution, the mixture made acid with hydrochloric acid to the desired acidity, and the whole shaken for 3-5 min. with an organic solvent. To obtain comparable results the amount of solvent was standardized at 2 ml.

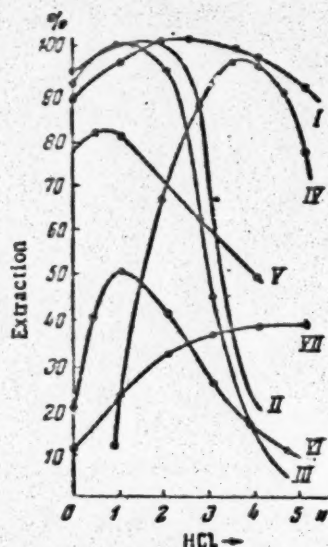


Fig. 1. Relationship between the degree of niobium extraction from solutions containing 2% ammonium bitartrate and the hydrochloric acid concentration. I) Chloroform; II) amyl acetate; III) diethyl ether; IV) isobutyraldehyde; V) benzaldehyde; VI) carbon tetrachloride; VII) cyclohexanone.

The volume of the aqueous phase was 13.5 ml (5 ml of the studied solution + HCl to give the desired acidity). As the solvent we used a number of organic compounds: chloroform, carbon tetrachloride, diethyl ether, ethyl acetate; the alcohols: n-butyl, isobutyl and isoamyl; isobutyraldehyde, n-heptane, o-xylene and benzene. Experiment revealed, as was to be expected, that not all of these solvents behaved the same in extracting the niobium cupferrate. The degree of extraction strongly depends on both the solvent nature and the solution acidity.

In Fig. 1 we show the results of a single extraction of niobium cupferrate by various solvents from solutions containing 2% ammonium bitartrate as a function of solution acidity. It can be seen from the figure that chloroform, ethyl acetate, diethyl ether and isobutyraldehyde are the best solvents for niobium cupferrate. Radioactive Nb^{95} was used to determine the completeness of extraction.

The above-mentioned organic solvents are also good solvents for the extraction of niobium cupferrate under other conditions (solutions containing ammonium binoxalate or ammonium bicarbonate, and also hydrochloric and sulfuric acid solutions).

The presence of foreign ions (alkali metals, NH_4^+ , NO_3^- , Cl^-), and raising the temperature to 25-30° do not show substantial influence on the degree of extraction.

Experiments run under similar conditions revealed that tantalum cupferrate is also easily extracted by organic solvents from acid solutions. Titanium, from both literature data [1,3] and our studies, in acid medium forms with cupferron a compound that is soluble in organic solvents. Consequently, the separation of these elements by the method of extracting the cupferrates from acid solutions proved impossible.

It seemed of interest to determine the possibility of extracting the cupferrates of niobium, tantalum and titanium from weakly acid, neutral and weakly alkaline solutions.

Extraction of Niobium, Tantalum and Titanium Cupferrates From Weakly Acid, Neutral and Weakly Alkaline Solutions. A. T. Pilipenko [6] developed a method for separating titanium from niobium and tantalum, based on the precipitation of the titanium at pH > 7 with cupferron from bitartrate solutions, and in that way confirmed the formation of titanium cupferrate at high pH values.

We studied the extraction of Nb, Ta and Ti cupferrates in the pH interval from 0 to 8. Experiment revealed that isoamyl alcohol is the most suitable solvent under these conditions; chloroform is also a good extractant here, but its volume has to be doubled.

The extraction is possible only from solutions containing 2-3% of ammonium bitartrate. Extraction is impossible when binoxalate and bicitrate solutions are used, since here precipitates insoluble in organic solvents are formed and the separation of the phases is a very slow operation.

The extraction was done as follows. To 3-5 ml of solution (concentration of oxides 0.7-0.8 mg/ml), placed in a separatory funnel, was added an equal volume of isoamyl alcohol and 0.5-0.8 ml of a 4% aqueous cupferron solution, and the whole shaken for 2-3 minutes; after separating the organic phase, the percent extraction of Nb and Ta was determined by the specific activity of the solution, while titanium was determined colorimetrically (after removing the solvent) by its reaction with H_2O_2 . The experimental results are plotted in Fig. 2, from which it can be seen that the degree with which niobium, tantalum and titanium cupferrates are extracted varies with the pH. This difference served as a base for the extraction method developed by us to separate titanium from niobium and tantalum.

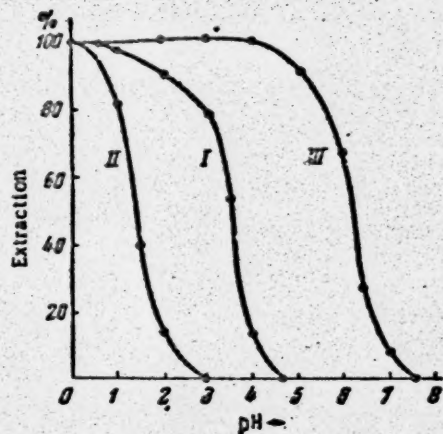


Fig. 2. Relationship between the degree of extraction of niobium (I), tantalum (II) and titanium (III) cupferrates by isoamyl alcohol and the pH.

(the pH was measured potentiometrically). Then various volumes (2-5 ml) of solution were removed and placed in a separatory funnel, an equal volume of isoamyl alcohol was added, then 0.5-1 ml of a 4% aqueous cupferron solution, and finally the mixture was shaken for 2-3 minutes. After this the organic layer was decanted and the extraction repeated 3 times.

Separation of Titanium From Niobium and Tantalum. When specimens containing niobium, tantalum and titanium are analyzed, these elements in most cases show mutual separation. Consequently, the problem reduces to the preliminary removal of titanium, which interferes with both gravimetric and colorimetric determinations of niobium and tantalum. The separation processes are quite complicated and do not always lead to satisfactory results.

We made a detailed study of the possibility of separating titanium by the method of extracting the cupferrates with isoamyl alcohol at pH 5 and obtained satisfactory results.

The separation of titanium was made from solutions containing $\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ and titanium in various proportions. The mixture of oxides (total 0.6-1.2 mg/ml) was fused with 8-10 weight parts of potassium pyrosulfate, the melt was dissolved in 2% ammonium bitartrate solution and the desired pH was established, using dilute NH_4OH .

TABLE 1

Separation of Titanium From Niobium and Tantalum

Taken, mg		$\frac{\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5}{\text{TiO}_2}$	Extracted, %	
$\frac{\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5}{\text{TiO}_2}$	TiO_2		TiO_2	$\frac{\text{Nb}_2\text{O}_5 + \text{Ta}_2\text{O}_5}{\text{TiO}_2}$
1.26	1.28	1:1	100	0
1.89	1.92	1:1	100	0
3.70	0.30	10:1	100	0
7.40	0.72	10:1	100	0
3.45	0.035	100:1	100	0
10.5	0.01	1000:1	100	0
0.35	3.5	1:10	100	0
0.01	1.0	1:100	100	0
0.001	5.0	1:5000	100	2

The completeness of separation was verified by reaction with H_2O_2 and by the use of the Nb^{94} and Ta^{182} isotopes. The activity was 2000-3000 imp/min per milliliter.

The separation results are given in Table 1. From the presented data it can be seen that titanium is completely separated from niobium and tantalum. Consequently, the method developed by us can be used to analyze specimens containing niobium, tantalum and titanium.

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STUDY OF THE STRUCTURE OF CELLULOSE BY THE ETHANOLYSIS METHOD

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Presented by Academician L. P. Barbin, March 7, 1958

Many chemical and physical properties of cellulose indicate the nonuniformity of its structure, explained by the simultaneous presence in it of disorderly (amorphous) and orderly (crystalline) regions. At the present time many different methods have been proposed [1-7] for the quantitative evaluation of these regions. All of these methods possess various essential limitations, in view of which the results obtained with their assistance vary within wide limits.

Thus, for example, the methods based on the reaction of cellulose with either thallium ethylate, organo-magnesium compounds, deuterium oxide or sorption of water vapors, give an idea as to the number of available hydroxyl groups present in cellulose, and which also belong to the loosely packed portion of the macromolecules found in the amorphous regions, and the hydroxyls located on the surface of the regions with a condensed, orderly structure.

Of greatest interest in this respect are the methods that are based on a measurement of the amount of readily hydrolyzable cellulose fraction. However, even these methods fail to give a true picture as to the amount of amorphous fraction due to the fact that the hydrolysis is accompanied by recrystallization of the disordered cellulose portions [8].

Another method deserving consideration is based on a determination of the amount of amorphous fraction from the specific gravity of the preparation. However, at the present time this method is also unsuitable for the measurements, since for subsequent calculations it is necessary to know the true specific gravities of both the amorphous and crystalline cellulose fractions. Unfortunately, a direct determination of these indices has not been accomplished up to now.

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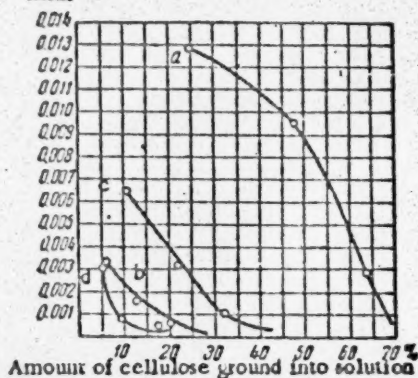


Fig. 1. Curves for the hydrolysis and ethanolysis of ground cellulose and viscose rayon. a) Ethanolysis of ground cellulose, b) hydrolysis of ground cellulose, c) ethanolysis of viscose rayon, d) hydrolysis of viscose rayon.

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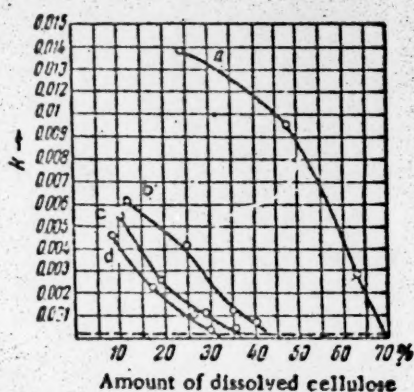


Fig. 2. Amount of amorphous fraction in recrystallized specimens of ground cellulose. a) Original ground cellulose, b) kept in water at 18°, c) kept in water at 100° for 1 hour, d) the same for 3 hours.

Striving to find a solution to the given problem, we attempted to replace the hydrolysis of cellulose by its ethanolysis in anhydrous medium. The exclusion of water from the system, being the source of cellulose recrystallization, could facilitate complete cleavage of the amorphous fraction.

To study this method we prepared an "amorphous" cellulose by grinding some cotton cellulose. The absolutely dry cellulose was ground for an hour in a special vibration mill with a steel cage, half-filled with steel balls. By means of a special mechanism the cage with the cotton cellulose was raised and dropped with an amplitude of 8 mm and a frequency of about 1000 vibrations a minute.

The x-ray pattern of such a cellulose showed one clearly defined amorphous ring of diffused light scattering. The alcoholysis of the ground cellulose was run in absolute alcohol, containing 10% of sulfuric acid monohydrate. The reaction was run in copper autoclaves, immersed in a boiling water bath. The duration of alcoholysis in individual experiments was 20, 60, 180 and 300 minutes.

On conclusion of reaction the autoclaves were cooled with cold water and their contents transferred to a glass filter, where the undissolved cellulose residue was washed with water until neutral and then dried to constant weight. From the weight loss suffered by the preparation during alcoholysis we calculated the minute cellulose solution rate constant for all of the investigated time intervals. On the basis of the data obtained in this manner we constructed the curves showing the relationship between the magnitude of the constant and the percent of dissolved substance.

The results of studying the ground cellulose preparation by this method are shown in Fig. 1, a. From the shape of the curve it can be seen that a considerable portion of the preparation dissolves very rapidly, apparently corresponding to alcoholysis of the amorphous fraction. After the cellulose reaches a certain solution point the rate of this process begins to decrease rapidly, in the end finally reaching the solution rate of difficultly hydrolyzable cellulose.

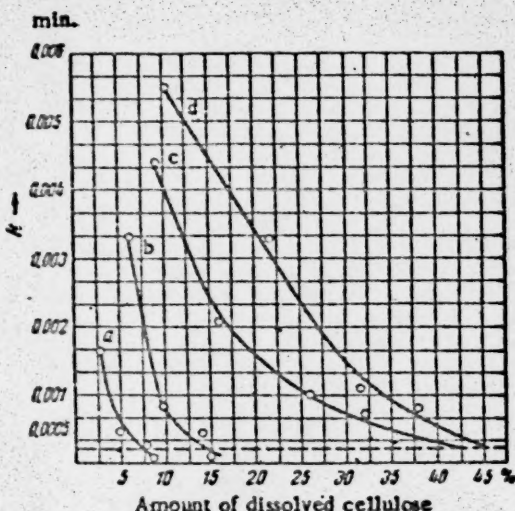


Fig. 3. Amount of amorphous fraction in various cellulose samples. a) Cotton cellulose, b) wood cellulose c) cellophane, d) viscose rayon.

line fractions, then the amount of readily reacting amorphous fraction in our studied pulverized cellulose specimen is about 68%.

When the ground cellulose is subjected to hydrolysis under similar conditions (Fig. 1, b) the attainment of the point corresponding to hydrolysis of the difficultly hydrolyzable portion of natural cellulose is observed at a considerably lower degree of solution for the preparation, which indicates the sharply damaging influence exerted by the recrystallization process in the given case.

A similar phenomenon, but on a considerably smaller scale, is observed in the comparative alcoholysis and hydrolysis of regenerated cellulose as viscose rayon. An examination of curves c and d (Fig. 1) shows that here also, due to recrystallization, the boundary of the difficultly hydrolyzable cellulose is reached considerably

The x-ray patterns of the cellulose residues after 20 minutes of either hydrolysis or ethanolysis showed that an interference pattern close to the x-ray pattern of natural cellulose, appears in the first case, while in the second case only small illumination of the diffusion ring is observed, apparently due to the accumulation of unchanged cellulose in the residue. Curve a in Fig. 1 also shows that the pulverized cellulose is heterogeneous and consists of a mixture of amorphous and crystalline fractions, showing sharply different capacities for ethanolysis. If the point (or a definite portion) for the transition of curve a into a straight line, corresponding to attainment of the ethanolysis rate for the main portion of natural cellulose, is tentatively taken as the boundary between the amorphous and crystal-

TABLE 1

Preparation No	Preparation	True specific gravity at 20°	% of amorphous cellulose from the density by the ethanolysis method		
			lit- er- a- ture	our data	
1	Ground cellulose, recrystallized with hot water	1.521	—	50	38
2	Cotton cellulose	1.542	42	18	7
3	Viscose rayon	1.523	76	47	45

Fig. 2. An analysis of this data clearly shows the influence of water as a powerful factor for the recrystallization of the amorphous fraction in cellulose. The amount of amorphous fraction in these samples equal to 68% in the original material, after treatment with cold water dropped to 43%, after 1-hour treatment with boiling water to 37%, and after 3-hour treatment with boiling water down to 30%. As a result, in its partial recrystallization the whole amorphous mass suffers condensation, which renders alcoholysis difficult.

The results of studying various samples of natural and regenerated cellulose by the alcoholysis method are plotted in Fig. 3. From the obtained data it follows that the amount of the amorphous fraction in cotton cellulose is about 7%, in spruce sulfite cellulose about 15%, in cellophane about 42%, and in viscose rayon about 45%.

A comparison of the alcoholysis and hydrolysis of spruce holocellulose under similar conditions gave practically identical results, indicating the absence of recrystallization phenomena in the process for the hydrolysis of the easily hydrolyzed polysaccharides found in the cell walls of plant tissue that had been made free of lignin.

This method also permits observing the rapid recrystallization shown by viscose rayon cellulose during the process of its very easy hydrolysis, proceeding almost without solution of the cellulose.

Extension of the ethanolysis method to a study of the structure shown by differently stretched viscose rayon samples revealed that here the amount of amorphous fraction is practically independent of the degree of stretch. For example, it was found that the fiber sample, stretched 10%, contains 48% amorphous fraction, while the sample with a 70% stretch shows a 50% content. These facts indicate that the fiber orientation due to stretching is different from the recrystallization process that is observed in the hydrolysis of the fiber with dilute acids. During stretching, together with increase in fiber orientation, a constant ratio of the amorphous and crystalline fractions is retained, while during hydrolysis this ratio shifts in the direction of increased crystalline fraction.

Having obtained with the alcoholysis method an approximate value for the amount of amorphous fraction present in ground cellulose, we next attempted to obtain a more accurate value for the specific gravity of the amorphous fraction. For this we used the flotation method in carbon tetrachloride to determine the true specific gravity of the ground cellulose, which proved to be 1.509. To determine the specific gravity of the crystalline portion in cellulose we measured this value for cotton cellulose that had been made free of the amorphous fraction by partial hydrolysis, which value proved to be 1.500, i.e., it was close to the calculated value of 1.558 obtained by Hermans [6]. Making use of the found specific gravity values and the ratio of the fractions, we calculated the specific gravity of the amorphous fraction, which proved to be 1.488, i.e., it was considerably smaller than the value calculated by Hermans (1.505). Making use of the found specific gravity values, we calculated the amount of amorphous fraction in various cellulose preparations.

Some of the obtained data are given in Table 1. An examination of the obtained results reveals that the values obtained by us for the amount of amorphous fraction by the method of specific gravities and ethanolysis are characterized by being considerably smaller than those obtained by other investigators.

* Here we define recrystallization as condensation of the cellulose and loss of its reactivity.

smaller in the hydrolysis of the preparation than in its alcoholysis.

Our theory that cellulose recrystallization* is responsible for the sharp difference in the hydrolysis and alcoholysis of various cellulose preparations could be verified by studying the ethanolysis rate of previously recrystallized cellulose preparations, containing substantial amounts of the amorphous fraction.

For this a sample of ground cellulose was kept in water for 1 hour at 18°, a second sample of the same cellulose was heated in water for 1 hour at 100°, and a third sample was kept in water at 100° for 3 hours. After this treatment the recrystallized preparations were washed with cold absolute alcohol to remove water, dried, and then subjected to alcoholysis. The obtained results are plotted in

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THERMAL STABILITY OF n-PARAFFIN HYDROCARBON COMPLEXES WITH UREA

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A. V. Topchlev

The complex-formation of urea with straight-chain aliphatic compounds (n-paraffins, alcohols, ketones), besides its practical value [1], is also of great scientific interest, since the crystalline molecular compounds that are formed here belong to the little studied type of so-called "inclusion complexes" [2,3]. An x-ray study of the structure of this type of complex revealed [4-6] that urea forms a hexagonal prism here, the interior of which can be regarded as being a peculiar canal with the dimensions in the widest part being about 6 Å, and in the narrowest about 5 Å. The paraffins with a straight-chain structure enter this canal in a stretched condition, forming the "inclusion complex".

Branched hydrocarbons with molecular cross sections close to or exceeding the value of the canal cross section cannot enter into the interior of the prism, and consequently fail to participate in the complex-formation reaction. At times an activator, most frequently either methyl alcohol or methyl ethyl ketone, is used to facilitate the start of the complex-formation reaction.

A study of the reaction of urea with individual paraffin hydrocarbons, in particular with n-octadecane, by the thermographic method [7] revealed that the solid molecular compound-complexes obtained here fail to melt, but instead decompose into the starting components, i.e., paraffin and urea, when heated to a certain temperature. The paraffins and urea are practically insoluble in each other, as a result of which the original paraffin can be quantitatively isolated from the complex after its decomposition. In this paper we give the results of our further study of the thermal stability shown by the complexes of a number of normal paraffin hydrocarbons, ranging from $C_{16}H_{34}$ to $C_{32}H_{66}$ inclusive. The differential-thermal method was used to make the study, with the N. S. Kurnakov pyrometer being used to obtain an automatic recording of the heating curves. The weight of sample taken for a recording was 0.06 g. The n-hydrocarbons used in the study were specially synthesized and were purified by repeated recrystallization from a number of solvents. The final recrystallization was made from ethyl alcohol.

The starting products for the synthesis of the hydrocarbons, the synthesis scheme, the elementary analysis of the hydrocarbons, and also the data obtained by the thermographic method on the melting points and polymorphic transformations, have all been described earlier [8].

The complexes of the indicated hydrocarbons were obtained in several ways: in the liquid phase by the method described by Bengen [9] and made more exact by us [10], and in the solid phase by grinding urea and the n-paraffin in an agate mortar either with or without the use of an activator. The obtained complexes were heated. It should be mentioned that the decomposition temperatures of the complexes formed in the solid and in the liquid phases are in good agreement between themselves, the difference being of the order of $\pm 0.5^\circ$.

The heating curves for the complexes of n-paraffins (from $C_{16}H_{34}$ to $C_{32}H_{66}$) with urea, prepared in the solid phase with the use of absolute methyl alcohol as the activator, are shown in Fig. 1. Several endothermic effects can be seen on the heating curves. The low-temperature effects correspond to phase transformations (polymorphous transformation, melting) [8] of the paraffin portion that had failed to participate in the complex-formation reaction. The endothermic effects located in the middle portion of the heating curves ($106.4-108.5^\circ$ for $C_{16}H_{34}$; $115.8-117.1^\circ$ for $C_{18}H_{38}$, etc.) belong to decomposition of the complexes, and finally the effect found at 134° on all of the heating curves corresponds to melting of the urea liberated in the decomposition of the complex.

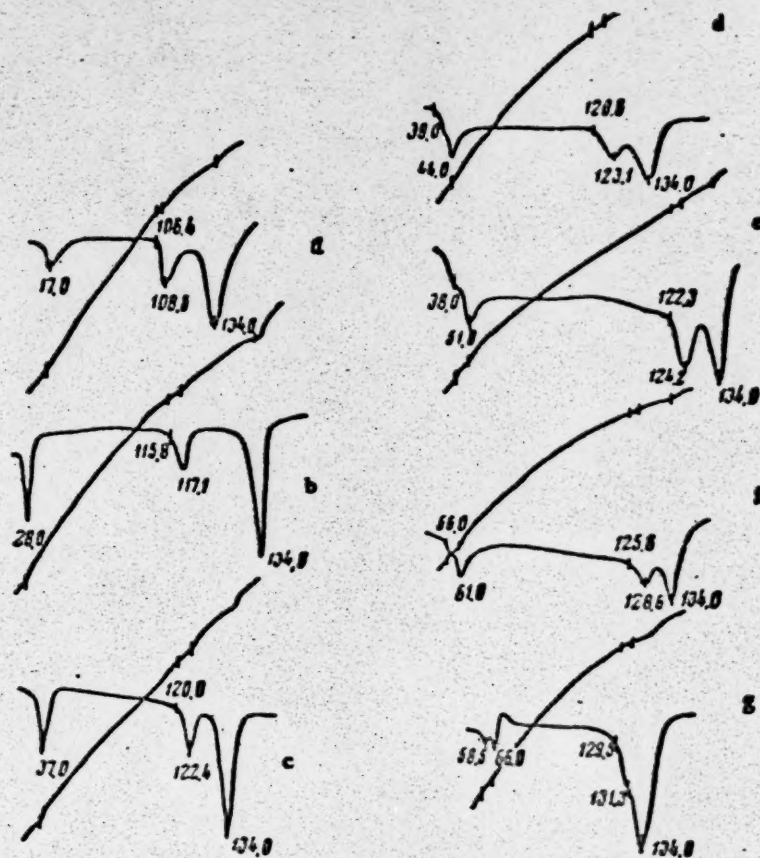


Fig. 1. Heating of the reaction products of n-paraffins with urea. a) $C_{16}H_{34}$, b) $C_{18}H_{38}$, c) $C_{20}H_{42}$, d) $C_{22}H_{46}$, e) $C_{24}H_{50}$, f) $C_{26}H_{54}$, g) $C_{28}H_{58}$, h) $C_{30}H_{62}$.

The effect for the decomposition of the complex was absent (the curve is not shown) on the heating curve of $C_{32}H_{66}$ with urea (when the reactants were reacted in the solid phase). In view of this we prepared the complex in the liquid phase by the method recommended by Bengen. Here the complex deposited as a voluminous precipitate. On its heating curve (Fig. 2 a) we observe the presence of the endothermic effects corresponding to the phase transformations of the unreacted paraffin, and then an unusually large effect for the melting of the urea. The increased area of the peak corresponding to urea melting can be explained by the presence of a substantial amount of free unreacted urea in the complex, and apparently, also by the fact that it corresponds to two merging processes: decomposition of the complex and melting of the urea. A slight inflection (point A) is observed on the differential curve, which can correspond to the end of the decomposition reaction for the complex, but its close proximity to the melting point of urea does not lend support to such an postulate. In order to make sure that the obtained precipitate is some sort of complex, the originally recorded specimen was kept in the recording block for 1 hour at the melting point, then cooled to room temperature, after which its heating curve was recorded again (Fig. 2 b). Here, as was to be expected, the size of the peaks on the differential curve, corresponding to melting of the paraffin, showed substantial increase when compared with the previous record (see Fig. 2 a), since here the paraffin liberated from the complex was combined with the unreacted paraffin. On the other hand, the peak corresponding to the melting of urea is smaller in size, since in this case the reaction for the decomposition of the complex is absent.

We also prepared the complexes of all of the hydrocarbons, with the exception of $C_{28}H_{58}$, $C_{30}H_{62}$ and $C_{32}H_{66}$ in the solid phase without the use of an activator. From Figs. 1 and 2 it follows that definite decomposition limits exist for the complexes of the hydrocarbons ranging from $C_{16}H_{34}$ to $C_{32}H_{66}$. More exact decomposition temperatures for the complexes were obtained by using a more accurate graduation in the individual recording of their heating curves. These results are shown in Table 1: It is possible that the temperature limits will vary somewhat as a

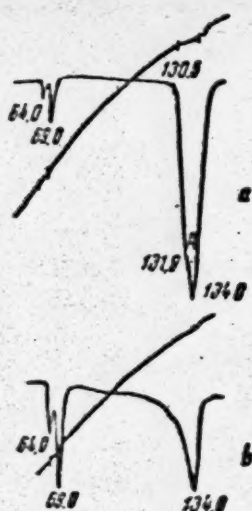


Fig. 2. a) heating of the $C_{25}H_{54}$ complex, b) its second heating after being kept in the block.

function of the rate of heating the complexes. In determining the decomposition temperatures a heating rate of 0.7-0.8° per minute for 0.06 g of sample was used.

Although the decomposition temperatures given for the complexes are quite close in some cases, still they are quite different between themselves and can be used to identify the complexes of both synthesized n-paraffins and those isolated from mixtures. As can be seen from the table, the decomposition temperature of the complexes increases as the number of carbon atoms in the chain of the normal paraffin increases. For the complexes of $C_{25}H_{52}$ and $C_{27}H_{54}$ it is very close to the melting point of urea. Proceeding from the structure of "inclusion complexes", it can be assumed that the compounds of urea with high-molecular hydrocarbons (above $C_{22}H_{46}$), if they are formed, should obviously decompose at the melting point of urea, i.e., at 133-134°.

In Fig. 3 we have plotted the temperature curves for the start and end of hydrocarbon-complex decomposition as a function of the number of carbon atoms in the chain. The curve shows an inflection at a point corresponding to the composition of a hydrocarbon close to $C_{25}H_{52}$. This situation coincides with the observations made by many investigators relative to the change occurring in the region of C_{22} and C_{23} for the regular progression of properties shown by even-numbered paraffins.

Thus, for example, Garner [11] derived an equation, linking the crystallization temperatures of n-hydrocarbons with the number of carbon atoms. The equation was used to calculate the crystallization points of the hydrocarbons from C_5H_{12} to $C_{70}H_{142}$. For the hydrocarbons above $C_{20}H_{42}$ the calculated and experimentally determined crystallization temperature values proved to be in good agreement. For the hydrocarbons with a shorter chain the theoretical values were considerably below the experimental. These facts can be explained if it is assumed that at room temperature the hydrocarbons below $C_{22}H_{46}$ show a crystalline structure, differing from the structures of $C_{22}H_{46}$, $C_{24}H_{50}$, etc.

Müller postulates [12] that with a certain chain length the end groups of the molecule will show a strong influence on the formation of a crystalline structure for the hydrocarbon, not playing this role in hydrocarbons with a long carbon chain. For odd-numbered hydrocarbons this influence, as he postulates, will show itself for members below C_6H_{14} and for the even-numbered series - in the hydrocarbons close to $C_{22}H_{46}$. As a result, the

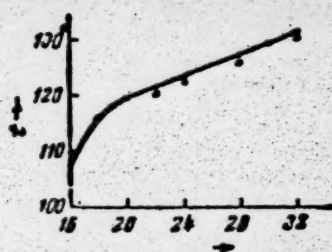


Fig. 3. Relationship between the incipient decomposition temperature t of complexes and the number n of carbon atoms in the n-paraffin chain.

TABLE 1

Hydrocarbon	Decomposition temperature limits in °C	Hydrocarbon	Decomposition temperature limits in °C
$C_{11}H_{24}$	106.4-108.5	$C_{21}H_{44}$	122.3-124.2
$C_{13}H_{28}$	115.8-117.4	$C_{23}H_{48}$	125.6-128.6
$C_{15}H_{32}$	120.0-122.4	$C_{25}H_{52}$	129.5-131.3
$C_{17}H_{36}$	120.6-123.1	$C_{27}H_{56}$	130.0-131.9

variation in the polymorphic modifications of the hydrocarbons entering into the composition of the complexes apparently exerts a substantial influence on their thermal stability.

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